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Proftest SYKE

FINAS Finnish Accreditation Service PT01 (EN ISO/IEC 17043)

Helsinki 2016
Finnish Environment Institute

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Finnish Environment Institute SYKE
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Layout: Markku Ilmakunnas

The publication is also available in the Internet: www.syke.fi/publication | helda.helsinki.fi/syke

ISBN 978-952-11-4654-1 (PDF)
ISSN 1796-1726 (Online)

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Publisher and financier of publication: Finnish Environment Institute (SYKE)
P.O. Box 140, FI-00251 Helsinki, Finland, Phone +358 295 251 000, syke.fi.

Year of issue: 2016

SYKE

ABSTRACT

Proftest SYKE arranged the proficiency test (PT) for measurement the gross and the net calorific value, the content of ash, carbon, nitrogen, hydrogen, moisture, sulphur and volatile matter in peat, wood pellet (not sulphur) and coal samples in September 2016. In total, there were 28 participants in the PT. Additionally, the participants were asked to estimate/calculate the emission factor for the peat and coal samples. In total, 90 % of the participants reported satisfactory results when the deviations of 1–30 % from the assigned values were accepted. In measurement of the gross calorific value from the peat sample 93 %, from the wood pellet sample 86 % and from the coal sample 84 % of the results were satisfactory. In measurement of the net calorific value from the peat sample 82 %, from the wood pellet 75 % and from the coal sample 85 % of the results were satisfactory.
The robust mean or mean of the reported results by the participants were used as the assigned values for measurements. The evaluation of performance was based on the z score which was calculated using the assigned value and the standard deviation for proficiency assessment at 95 % confidence level. The evaluation of performance was not done for the measurement of moisture in all samples, emission factor in peat samples and nitrogen in wood pellet samples.
Warm thanks to all the participants of this proficiency test!

Keywords: Proficiency test, interlaboratory comparison, coal, peat, wood pellet, calorific value, emission factor, ash, moisture, carbon, sulphur, nitrogen, hydrogen, volatile matter, environmental laboratories

TIIVISTELMÄ

Proftest SYKE järjesti syyskuussa 2016 pätevyyskokeen kalorimetrisen ja tehollisen lämpöarvon sekä tuhkan, vedyn, typen, rikin, haihtuvien yhdisteiden ja kosteuden määrittämiseksi turpeesta, puupelletistä (ei rikkiä) ja kivihiilestä. Lisäksi osallistujilla oli mahdollisuus arvioida/laskea turve- ja kivihiilinäytteiden päästökerroin. Pätevyyskokeessa oli yhteensä 28 osallistujaa. Koko tulosaineistossa hyväksyttäviä tuloksia oli 90 %, kun vertailuarvosta sallittiin 1–30 % poikkeama. Kalorimetrisen lämpöarvon tuloksista oli hyväksyttäviä 93 % (turve), 86 % (puupelletti) ja 84 % (kivihiili). Tehollisen lämpöarvon tuloksille vastaavat hyväksyttävien tulosten osuudet olivat 82 % (turve), 75 % (puupelletti) ja 85 % (kivihiili).
Pätevyyden arviointi tehtiin z-arvojen avulla ja niiden laskemisessa käytetyn kokonaishajonnan tavoitearvot olivat välillä 1–30 %. Mittaussuureen vertailuarvona käytettiin osallistujien ilmoittamien tulosten robustia keskiarvoa tai keskiarvoa. Tulosten arviointia ei tehty testinäytteiden kosteuspitoisuuden määritykselle, turpeen päästökertoimen laskennalle ja typen määritykselle puupelletistä.
Kiitos pätevyyskokeen osallistujille!

Avainsanat: pätevyyskoe, vertailumittaus, kalorimetrinen lämpöarvo, tehollinen lämpöarvo, päästökerroin, tuhka, kosteus, hiili, rikki, typpi, haihtuvat yhdisteet ja vety, turve, puupelletti, hiili, ympäristölaboratoriot

SAMMANDRAG

Proftest SYKE genomförde i september 2016 en provningsjämförelse som omfattade bestämningen av kalorimetriskt och effektivt värmevärde, svavel, väte, kol, kväve, askhalt, flykthalt och fukthalt i torv, träd pellet (inte svavel) och stenkol. Det var en möjlighet att beräkna emissionfaktor i torv och stenkol prover. Totalt 28 deltagarna deltog i jämförelsen.
Som referensvärde för analyternas koncentration användes mest det robusta medelvärdet av deltagarnas resultat. Resultaten värderades med hjälp av z-värden. I jämförelsen var 90 % av alla resultaten acceptabel, när en total deviation på 1–30 % från referensvärdet tilläts. Av det kalorimetriska värmevärdet var 93 % acceptabla (torv), 86 % (träd pellet) och 84 % (stenkol). För resultaten av det effektiva värmevärdet var 82 % (torv), 75 % (träd pellet) och 85 % (stenkol) acceptabla. Det var inte gjorts värdering till fuktighalt i alla prover, beräkning av emissionfaktor i torv provet och kväve i träd pellet.
Ett varmt tack till alla deltagarna i testet!

Nyckelord: provningsjämförelse, kalorimetriskt och effektivt värmevärde, emissionfaktor, svavel, väte, kol, nitrogen, askhalt, flykthalt fukthalt stenkol, torv, träd pellet, miljölaboratorier

CONTENTS

1 Introduction

Proftest SYKE carried out the proficiency test (PT) for analysis of gross and net calorific value in fuels (CAL 08/2016) in September 2016. In total there were 28 participants in the PT. Gross and net calorific value, carbon, sulphur, hydrogen, nitrogen, moisture content of the analysis sample (M_{ad}), ash content, and volatile matter (V_{db}) were tested in peat, wood pellet (not sulphur) and coal samples.

Finnish Environment Institute (SYKE) is appointed National Reference Laboratory in the environmental sector in Finland. The duties of the reference laboratory include providing interlaboratory proficiency tests and other comparisons for analytical laboratories and other producers of environmental information. This proficiency test has been carried out under the scope of the SYKE reference laboratory and it provides an external quality evaluation between laboratory results, and mutual comparability of analytical reliability. The proficiency test was carried out in accordance with the international guidelines ISO/IEC17043 [1], ISO 13528 [2] and IUPAC Technical report [3]. The Proftest SYKE has been accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi/Documents/PT01_M08_2016.pdf). The organizing of this proficiency test is included in the accreditation scope of the Proftest SYKE.

2 Organizing the proficiency test

2.1 Responsibilities

Organizer:

Proftest SYKE, Finnish Environment Institute (SYKE), Laboratory Centre
Hakuninmaantie 6, FI-00430 Helsinki, Finland
Phone: +358 295 251 000
E-mail: proftest@environment.fi

The responsibilities in organizing the proficiency test were as follows:

Mirja Leivuori	coordinator
Riitta Koivikko	substitute of coordinator
Keijo Tervonen	technical assistance
Markku Ilmakunnas	technical assistance
Sari Lanteri	technical assistance

Partner:

Minna Rantanen from Ramboll Finland Oy (Vantaa) was participating in organizing the proficiency test as well as acting analytical expert.

Subcontracting:
Testing of samples Ramboll Finland Oy (T039 accredited by FINAS, www.finas.fi/Documents/T039_Liite1_01_M30_2016.pdf)

2.2 Participants

In total 28 participants took part in this proficiency test, of which 11 were from Finland and 17 from other countries (Appendix 1). One participant registered for the test only on 28 September 2016, which was the deadline for result reporting. As the samples are known to be well stable, the registration was accepted and the samples were delivered for them separately. In the final data handling the results of the late registered participant were treated as manual outliers, thus these results were not included in the statistical data handling and they have no influence to the performance evaluation of the other participants.

Altogether 75 % of the participants used accredited analytical methods at least for a part of the measurements. The samples were tested at the laboratory of Ramboll Finland Oy in Vantaa and their participant code is 1 in the result tables.

2.3 Samples and delivery

Three different fuel samples were delivered to the participants: peat, wood pellet and coal samples. Gross ($q_{V,gr,d}$) and net ($q_{p,net,d}$) calorific value, C, S, H, N, moisture content of the analysis sample (M_{ad}), ash content, and volatile matter (V_{db}) were tested in peat, wood pellet (not sulphur) and coal samples.

This PT used the samples from the previous PT CAL 06/2012 [4]. The samples were homogenated and divided again in the laboratory of Proftest SYKE. The samples were tested at the laboratory of Ramboll Finland in Vantaa.

The material for the peat sample (B1) was collected from the Finnish marshland. The raw material for wood pellets (B2) was naked softwood (spruce and pine) sawdust and molding shavings. The coal sample (K1) was prepared from a Russian steam coal. The sample preparation is described in details in the report of the PT CAL 06/2012 [4].

In the cover letter delivered with the samples, the participants were instructed first to store the samples closed for one day after their arrival and then to measure the moisture content of the analysis sample (M_{ad}) as the first measurement. The samples were instructed to be homogenized before measurements and to be stored in a dry place at room temperature. Further, the moisture content of the analysis sample was instructed to be measured on every day of measurements. This was important as it eliminates the influence of humidity on the measurements. The participants were also asked to report the relative humidity (%) of the measuring room as an average of the measuring dates.

The participants had the possibility to estimate/calculate the emission factor (as received) for peat and coal samples. For this estimation/calculation, the total moisture contents of the samples as received (M_{ar}) were given:

- peat B1 45.5 %,
- coal K1 10.3 %

The samples were delivered on 6 September 2016 to the participants. The samples arrived to the participants mainly on the 9 September 2016. Participant 20 received the samples on 20 September 2016.

The samples were requested to be measured and to be reported latest on 28 September 2016. One participant delivered the results one day later. The preliminary results were delivered to the participants via ProftestWEB and email on 5 October 2016. Late registered participant reported results on 14 October 2016 and they got preliminary results via email on 19 October 2016.

2.4 Homogeneity

Homogeneity of the samples B1, B2 and K1 was tested as duplicate determinations from two subsamples (Appendix 2). The number of testing items was reduced as the tested materials were used in the previous PT CAL 06/2012 [4]. According to the homogeneity test results, all samples were considered homogenous. Based on the knowledge of the provider the samples have been considered stabile during the test.

2.5 Feedback from the proficiency test

The feedback from the proficiency test is shown in Appendix 3. The comments from the participants mainly dealt with delivering delays and reporting errors with the samples. The comments from the provider are mainly focused to the lacking conversancy to the given information with the samples. All the feedback is valuable and is exploited when improving the activities.

2.6 Processing the data

2.6.1 Pretesting the data

The normality of the data was tested by the Kolmogorov-Smirnov test. The outliers were rejected according to the Grubbs or Hampel test before calculating the mean. Also before the statistical calculation some outliers were rejected in case that the results deviated from the robust mean more than 50 % or 5 times robust standard deviation or anomalous values in the measured element value were used in the calculation. The rejection of results was partly based to the rather strict requirements for the reproducibility given in the standards for analysis described in the covering letter of the samples. The duplicate results were tested using the Cochran test. If the result was reported lower than detection limit, it was not included in calculations.

More information about the statistical handling of the data is available in the Guide for participant [5].

2.6.2 Assigned values

Mainly the robust mean was used as the assigned value for measurements of the test samples, when there were at least 12 results ($n \geq 12$). Also the mean value and the median value (after Grubbs or Hampel outlier test) of the data were calculated, which were quite similar to the assigned values (Table 1). In cases, where the number of results was lower than 12, the mean value of participants' results was used as the assigned value (B1, B2, K1: H_d, N_d, $q_{p,net,d}$, V_{dp}; B1, B2: C_d; B1,K1: EF; B1: S_d).

The robust mean (or mean) is not metrologically traceable assigned value. As it was not possible to have metrologically traceable assigned values, the robust means (or means) of the results were the best available values to be used as the assigned values. The reliability of the assigned value was statistically tested [2, 3].

When the robust mean was used as the assigned value, the expanded measurement uncertainty was calculated using the robust standard deviation. When the mean value was used as the assigned value, the expanded measurement uncertainty was estimated based on the standard deviation [2, 5]. When using the robust mean or mean of the participant results as the assigned value, the standard uncertainties of the assigned values for calorific values were between 0.1 % and 0.4 %. For the other evaluated measurands the uncertainty varied from 0.4 % to 9.6 % (Appendix 4).

The participants also calculated emission factors (EF) for the peat and coal samples according to the given total moisture contents as received (M_{ar}). In this PT, due the low number of the results and the variability between the emission factor results the performance evaluation is done only for coal sample (K1) and the performance evaluation is only indicative. The number of the nitrogen results was too low for the performance evaluation in wood pellet sample (B2, Table 1). Further, there was high variation in the results of analysis moisture (M_{ad}), thus the results have not been evaluated, but the assigned values are presented (Table 1).

After reporting the preliminary results no changes have been done for the assigned values.

2.6.3 Standard deviation for proficiency assessment and z score

The requirements for the reproducibility of the used standard methods were reported in the cover letter delivered with the samples and they were used to estimate the standard deviation of the proficiency assessment in PT. The reproducibility required in the standard methods was mainly fulfilled for gross calorific values. The target value for the standard deviation for the proficiency assessment ($2 \times s_{pt}$ at the 95 % confidence level) was set to 1–30 % depending on the measurements.

The reliability of the assigned values was tested according to the criterion $u_{pt} / s_{pt} \leq 0.3$, where u_{pt} is the standard uncertainty of the assigned value and s_{pt} is the standard deviation for proficiency assessment [3]. When testing these reliabilities the criterion was mainly fulfilled and the assigned values were considered reliable.

The reliability of the target value of the standard deviation for proficiency assessment and the corresponding z score was estimated by comparing the deviation for proficiency assessment (s_{pt}) with the robust standard deviation or standard deviation of the reported results (s_{rob}) [3]. The criterion $s_{rob} / s_{pt} < 1.2$ was mainly fulfilled.

Only for hydrogen in peat sample (B1) the criterion for the reliability of the assigned value and the reliability of the standard deviation for proficiency assessment was not totally fulfilled. In this PT the number of the results was low, and thus the evaluation was compared to the evaluation of the same measurand and test material in the previous round CAL 06/20152 [4], which confirmed the appointed assigned value and standard deviation for performance assessment.

After reporting the preliminary results no changes have been done for the standard deviation for proficiency assessment.

3 Results and conclusions

3.1 Results

The summary of the results of this proficiency test is presented in Table 1. Explanations to terms used in the result tables are presented in Appendix 5.The results and the performance of each participant are presented in Appendix 6. The reported results with their expanded uncertainties (k=2) are presented in Appendix 7. The summary of the z scores is shown in Appendix 8 and z scores in the ascending order in Appendix 9.

The robust standard or standard deviations of the results mainly varied from 0.3 to 16.2 % (Table 1). The robust standard or standard deviation was lower than 2 % for 50 % of the results and lower than 6 % for 85 % of the results (Table 1, Appendix 6). The robust standard deviation of the results was higher than 6 % for moisture (B1, K1), sulphur (B1) and for ash it was the highest 16.2 % (B2, Table 1). For nitrogen in the wood pellet sample the robust standard deviation (58.8 %) indicate high variation within the low concentration level, and thus nitrogen was not evaluated (Table 1). The robust standard or standard deviations were approximately within the same range as in the previous similar proficiency test CAL 06/2015, where the deviations varied from 0.3 % to 12.1 % [6].

Table 1. The summary of the results in the proficiency test 08/2016.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	SD rob	SD rob %	2 x s_{pt} %	n (all)	Acc z %
Ash_d	B1	w%	7.11	7.11	7.11	7.19	0.22	3.2	6	15	100
	B2	w%	0.30	0.30	0.30	0.31	0.05	16.2	30	19	95
	K1	w%	13.3	13.3	13.3	13.3	0.1	1.0	2.5	19	89
C_d	B1	w%	54.4	54.4	54.3	54.4	0.5	0.9	3	8	88
	B2	w%	50.6	50.6	50.6	50.7	0.4	0.7	2.5	12	92
	K1	w%	69.3	69.3	69.3	69.3	0.5	0.7	2.5	14	93
EF	B1	t CO2/TJ	106	106		106			-	6	-
	K1	t CO2/TJ	93.9	93.9	93.8	93.2	1.7	1.8	4	10	100
H_d	B1	w%	5.62	5.62	5.64	5.65	0.28	5.0	7	7	86
	B2	w%	6.03	6.03	6.03	6.03	0.17	2.8	6	11	73
	K1	w%	4.59	4.59	4.59	4.61	0.14	3.1	6	12	92
$M_{ad,d}$	B1	w%	7.40	7.40	7.40	7.36	0.46	6.2	-	12	-
	B2	w%	7.59	7.59	7.59	7.58	0.21	2.8	-	17	-
	K1	w%	3.79	3.80	3.79	3.79	0.29	7.6	-	18	-
N_d	B1	w%	1.83	1.83	1.83	1.85	0.04	2.3	10	7	100
	B2	w%	0.07	0.07	0.10	0.07	0.06	58.8	-	10	-
	K1	w%	2.23	2.23	2.26	2.29	0.13	5.6	10	10	90
$q_{p,net,d}$	B1	J/g	20768	20768	20792	20784	65	0.3	1.7	11	82
	B2	J/g	18885	18885	18892	18906	65	0.3	1.8	16	75
	K1	J/g	27513	27513	27513	27571	167	0.6	1.2	13	85
$q_{V,gr,d}$	B1	J/g	22035	22034	22035	22037	120	0.5	1.3	14	93
	B2	J/g	20216	20216	20216	20220	95	0.5	1.5	21	86
	K1	J/g	28542	28533	28542	28581	119	0.4	1.0	19	84
S_d	B1	w%	0.20	0.20	0.20	0.20	0.02	10.7	20	10	100
	K1	w%	0.46	0.46	0.46	0.46	0.02	5.2	15	17	100
V_{db}	B1	w%	66.1	66.1	66.2	66.1	0.6	1.0	3	8	88
	B2	w%	85.0	85.0	85.0	85.0	0.6	0.7	3	10	90
	K1	w%	34.8	34.8	34.9	35.0	0.7	2.0	3	15	87

Rob. mean: the robust mean, SD rob: the robust standard deviation, SD rob %: the robust standard deviation as percent, $2 \times s_{pt}$ %: the standard deviation for proficiency assessment at the 95 % confidence interval, Acc z %: the results (%), where $|z| \leq 2$, n(all): the total number of the participants.

In this proficiency test the participants were requested to report the replicate results for all measurements. The results of the replicate determinations based on the ANOVA statistics are presented in Table 2. The international standards related to the measurements of fuels recommend the target values for the repeatability.

In particular, in measurements of the calorific values, the requirement for the repeatability is ± 120 J/g. In this proficiency test the requirements for the repeatability of the measurements of the gross calorific value were 0.54 % for the sample B1, 0.59 % for the sample B2 and 0.42 % for the sample K1 and in measurements of the net calorific value 0.58 %, 0.64 % and 0.44 %, respectively. In each case, the obtained repeatability of the measurement of the gross calorific value and the net calorific value was lower than the repeatability requirement (Table 2, the column s_w %).

The estimation of the robustness of the methods could be done by the ratio s_b/s_w. The ratio s_b/s_w should not exceed the value 3 for robust methods. Here, however, the robustness exceeded the

value 3 in many cases (Table 2). For the gross calorific value the ratio s_b/s_w was 1.3 (the sample B1), 5.2 (B2) and 5.1 (K1) and for the net calorific value the ratio was 2.6, 3.7 and 6.1, respectively. For the calorific values the ratio s_b/s_w was mainly within the same range than in the previous similar proficiency test CAL 06/2015, with the exception of the lower ratio for the peat sample (B1) [5].

Table 2. The summary of repeatability on the basis of replicate determinations (ANOVA statistics).

Measurand	Sample	Unit	Assigned value	Mean	s_w	s_b	s_t	s_w%	s_b%	s_t%	s_b/s_w
Ash_d	B1	w%	7.11	7.11	0.054	0.197	0.205	0.76	2.8	2.9	3.6
	B2	w%	0.30	0.30	0.023	0.042	0.0490	8.2	14	16	1.7
	K1	w%	13.3	13.3	0.052	0.155	0.163	0.39	1.2	1.2	3.0
C_d	B1	w%	54.4	54.4	0.081	1.76	1.77	0.15	3.3	3.3	22
	B2	w%	50.6	50.6	0.203	0.426	0.472	0.40	0.84	0.93	2.1
	K1	w%	69.3	69.3	0.163	0.705	0.724	0.24	1.0	1.0	4.3
EF	B1	t CO2/TJ	106	106	0.206	0.466	0.510	0.19	0.44	0.48	2.3
	K1	t CO2/TJ	93.9	93.9	0.287	1.70	1.72	0.31	1.8	1.8	5.9
H_d	B1	w%	5.62	5.62	0.029	0.283	0.284	0.52	5.0	5.1	9.8
	B2	w%	6.03	6.03	0.029	0.223	0.225	0.49	3.7	3.7	7.6
	K1	w%	4.59	4.59	0.021	0.132	0.134	0.45	2.9	2.9	6.5
$M_{ad,d}$	B1	w%	7.40	7.40	0.071	0.402	0.409	0.95	5.4	5.5	5.7
	B2	w%	7.59	7.59	0.048	0.415	0.417	0.63	5.5	5.5	8.7
	K1	w%	3.79	3.80	0.058	0.705	0.707	1.5	19	19	12
N_d	B1	w%	1.83	1.83	0.012	0.052	0.054	0.67	2.9	3.0	4.3
	B2	w%	0.07	0.07	0.008	0.053	0.054	8.3	53	54	6.4
	K1	w%	2.23	2.23	0.028	0.186	0.188	1.2	8.1	8.2	6.6
$q_{p,net,d}$	B1	J/g	20768	20768	31.3	80.3	86.2	0.15	0.39	0.41	2.6
	B2	J/g	18885	18885	19.4	70.9	73.5	0.10	0.38	0.39	3.7
	K1	J/g	27513	27513	24.1	147	149	0.088	0.54	0.54	6.1
$q_{V,gr,d}$	B1	J/g	22035	22034	73.9	93.7	119	0.34	0.43	0.54	1.3
	B2	J/g	20216	20216	57.7	299	305	0.29	1.5	1.5	5.2
	K1	J/g	28542	28533	24.1	123	125	0.085	0.43	0.44	5.1
S_d	B1	w%	0.20	0.20	0.0061	0.018	0.019	3.1	9.2	9.6	3.0
	K1	w%	0.46	0.46	0.0082	0.022	0.024	1.8	4.8	5.1	2.7
V_{db}	B1	w%	66.1	66.1	0.170	0.983	0.997	0.26	1.5	1.5	5.8
	B2	w%	85.0	85.0	0.140	0.528	0.546	0.16	0.62	0.64	3.8
	K1	w%	34.8	34.8	0.086	0.639	0.644	0.25	1.8	1.8	7.5

Ass.val.: assigned value; s_w**:** repeatability standard error; s_b**:** between participants standard error; s_t**:** reproducibility standard error.

3.2 Analytical methods

The participants were allowed to use different analytical methods for the measurements in the PT. A questionnaire of some detailed information related to the used analytical methods was provided along the proficiency test. The summary of the answers is shown in Appendix 10. The statistical comparison of the analytical methods was possible for the data where the number of the results was ≥ 5. In some cases there were not enough results for statistical comparison and in those cases the comparison is based on the graphical result evaluation. The noticed significant difference is shown in Appendix 11. The used analytical methods and the results of the participants grouped by methods are shown in more detail in Appendix 12.

3.2.1 Gross and net calorific value

The analytical methods based on different standard methods were used for the measurements in the proficiency test. The used analytical methods of the participants are shown in more detail in Appendix 12.

Mostly, standard methods were used for measurement of calorific value (EN 14918 [7], ISO 1928 [8]. Only one participant used technical speciation (CEN/TS 15400, participant 21). The participants used mostly 0.8–2.5 g of sample for the measurements of the calorific value. The measurements of calorific value were done by PARR, IKA or LECO equipment (Appendix 10).

In the calculations of gross calorific value ($q_{V,gr,d}$), various correction factors were used. Fuse wire, ignition, acid, moisture, nitrogen and sulphur corrections were most commonly used in several different combinations depending of the test material (Appendix 10). For the calculation of net calorific value ($q_{p,net,d}$), different combinations of correction factors were used as well depending of the test material (Appendix 10). Mainly nitrogen plus oxygen and hydrogen content was used for corrections. Based on the graphical result evaluation, clear differences between the used methods in gross and net calorific value measurements could not be concluded.

3.2.2 Measurement of carbon, hydrogen, nitrogen, sulphur, moisture, ash, and volatile matter

In the proficiency test the following several standard methods or technical specifications were mainly used for measurements of different parameters:

Measurand	Method
C, H and N	EN 15104 [9], ISO 29541 [10], ASTM D 5373 [11], EN ISO 16948 [12]
S	EN 15289 [13], EN ISO 16994 [14], ASTM D 4239 [15]
Analytical moisture content	EN 14774-3 [16], ISO 589 [17], DIN 51718 [18], ASTM D 7582 [19], ASTM D 5142 [20], EN ISO 18134 [21], ISO 11722 [22]
Ash content	EN 14775 [23], ISO 1171 [24], ASTM D 7582 [19], ASTM D 5142 [20], EN ISO 18122 [25]
Volatile matter	EN 15148 [26], ISO 562 [27], EN ISO 18123 [28]

However, in some cases also other international and national standards or technical speciation (e.g. CEN/TS 1503, CEN/TS 15414-3, CEN/TS 15402, ASTM D 5142) or internal methods (e.g. participants 2, 9, 15, 16, 19, 20, 21) were used. Moisture content was mainly determined gravimetrically by heating in air or N_2 atmosphere at the temperatures of 103-107.5 °C. Moisture content was measured also using TGA at the temperatures of 105-107 °C. Air and N_2 atmosphere was used for determining moisture content for coal samples. One participant used nitrogen atmosphere for the wood pellet sample (Appendix 10).

The ash content was determined mainly gravimetrically by heating at the temperature 550 °C (Samples B1, B2) or at the temperature 815 °C (Sample K1). Ash content was measured also using TGA for samples at the temperatures 250+550°C, 550 °C, 750 °C or 815 °C (Appendix 10). The statistical comparison of the analytical methods showed differences in the ash measurements between standards EN 14775 and EN ISO 18122 (Appendix 11). For the other measurands no differences were noticed.

In the proficiency test also information of detection limit of nitrogen and sulphur was collected (Appendix 10). The reported detection limits varied from 0.01 to 0.05 w% for nitrogen and from 0.001 to 0.1 w% for sulphur.

3.3 Measurement uncertainties of the results

In total 76 % of the participants reported the expanded uncertainties (k=2) with their results for at least some of their results (Table 3, Appendix 13). The range of the reported uncertainties varied between the measurements and the sample types.

Several approaches were used for estimating of measurement uncertainty (Appendix 13). The most used approach was based on method validation data or the internal quality data with or without the results obtained in proficiency test. One to three participants reported the usage of the MUkit measurement uncertainty software for the estimation of their uncertainties [29]. The free software is available in the webpage: www.syke.fi/envical/en. Generally, the used approach for estimating measurement uncertainty did not make definite impact on the uncertainty estimates.

The estimated uncertainties varied highly for all the tested measurements (Table 3). Especially, very low or high uncertainties can be considered questionable. Also measurement uncertainty could not be zero as one participants reported. It was evident, that some uncertainties had been reported erroneously for the measurands (including calorific values, Appendix 13), not as relative values as the provider of this proficiency test had requested.

Table 3. The range of the expanded measurement uncertainties (k=2, U_i%) reported by the participants.

Measurement	U_i %, B1	U_i %, B2	U_i %, K1
Ash	0.13-10	0.05-48	0.03-6
C	0.4-5.5	0.15-40	0.1-5
EF	3-10	-	2-6.2
H	0.85-16	0.15-10	0,19-10
N	0.81-25	0.15-30	0.20-38
q-p,net,d	0.9-5	0-92	0.23-92
q-V,gr,d	0.9-5	0.33-120	0.12-120
S	4.2-30	-	0.05-14
V_{db}	0.13-5	0.13-10	0.03-5

3.4 Estimation of emission factor

Additionally, the participants were asked to estimate the emission factors for the peat and coal samples distributed in the proficiency test by taking into account their own net calorific values and the total moisture values as received, which was informed in the cover letter of the samples. The calculation of the emission factor of the wood pellet sample (B2) was not done as it is a CO_2 neutral fuel. In this PT, due the low number of the results and the variability between the emission factor results the performance evaluation is done only for coal sample (K1) and the performance evaluation is only indicative. Based on the data it seems that some participants (e.g. participant 5) might has calculated emission factor for coal using the moisture content of the analysis sample (M_{ad}).

4 Evaluation of the results

The evaluation of the participants was based on the z scores, were calculated using the assigned values and the standard deviation for performance assessments (Appendix 5). The z scores were interpreted as follows:

Criteria	Performance
$\lvert z \rvert \leq 2$	Satisfactory
$2 < \lvert z \rvert < 3$	Questionable
$\lvert z \rvert \geq 3$	Unsatisfactory

In total, 90 % from the results were satisfactory when deviations of 1–30 % from the assigned values were accepted. About 75 % of the participants used the accredited methods and 92 % of their results were satisfactory. Proftest SYKE arranged a similar proficiency test in 2015 and then 85 % of the results were satisfactory [6].

The summary of the performance evaluation is shown in Table 4. The percentage of the satisfactory results varied between 82 % and 91 % for the tested sample types (Table 4). The criteria for performance had been mainly set according to the target value for reproducibility recommended in international standards or technical specifications for measurement of the

Table 4. Summary of the performance evaluation in the proficiency test CAL 08/2016.

Sample	Satisfactory results (%)	Accepted deviation from the assigned value (%)	Remarks
Peat, B1	82	1.3-20	• In the CAL 06/15 the performance was satisfactory for 86 % of the results [6].
Wood pellet, B2	85	1.5-30	• Difficulties in measurements for H_d and net calorific value in which there were < 80% satisfactory results. In the CAL 06/15 the performance was satisfactory for 82 % of the results [6].
Coal, K1	91	1-15	• Good performance. In the CAL 06/15 the performance was satisfactory for 87 % of the results [6].

calorific values and other determinants. The reproducibility required in the standards was fulfilled for the gross calorific values. For the net calorific value increased reproducibility from the value for the gross caloric value was used. There was no criterion for reproducibility for the net calorific value in standards methods.

Peat

In the previous similar proficiency test CAL 06/15 the satisfactory results of the peat sample (B1) were in total 86 % [6], thus the performance in this PT is slightly declined (82 %, Table 4). The satisfactory results varied between 82 % (net calorific value) and 100 % (ash, N, S) for the peat sample (Table 1). In this proficiency test the number of satisfactory results of the gross values was in the same level (82 %) and the net calorific values (93 %) for the peat sample was higher than in the previous proficiency test CAL 06/15 (82 % and 86 %, respectively) [6]. The results of analysis moisture (M_{ad}) and emission factor have not been evaluated, but the assigned values are presented (Table 1).

Wood pellet

In the previous similar proficiency test CAL 06/15 the satisfactory results of the wood pellet sample (B2) were in total 82 % [6], thus the performance in this proficiency test was somewhat better (85 %, Table 4). The satisfactory results varied between 73 % (H) and 95 % (Ash) for the wood pellet sample (Table 1). The number of nitrogen result was too low for the performance evaluation in peat sample (B2, Table 1). In the measurement of gross and net calorific values, 75 % and 86 %, respectively, were satisfactory when accepting deviations of 1.5 % and 1.8 % from the assigned values (Table 1). The number of satisfactory results of the gross and net calorific values for wood pellet was lower for gross calorific value and higher for the net calorific value than in the previous proficiency test CAL 06/15 (85 % and 72 % respectively) [6]. The estimation of EF was not done as it is a CO_2 neutral fuel. Also the results of analysis moisture (M_{ad}) have not been evaluated, but the assigned value is given (Table 1).

Coal

In the previous similar proficiency test CAL 06/15 the satisfactory results of the coal sample (K1) were in total 87 % [6], thus the performance was enhanced in this PT (91 %, Table 4). In

the measurement of gross and net calorific values, 85 % and 84 % of results, respectively, were satisfactory, when accepting the deviations of 1 and 1.2 % from the assigned values (Table 1). In this proficiency test the number of satisfactory result of the gross and net calorific values were nearly in the same range than in the previous test CAL 06/15 (85 % and 81 %, respectively) [6]. The results of analysis moisture (M_{ad}) have not been evaluated, but the assigned value is given (Table 1).

5 Summary

Proftest SYKE carried out the proficiency test (PT) for the analysis of the gross and the net calorific value as well as for content of ash, carbon, hydrogen, nitrogen, sulphur, analytical moisture content and volatile matter in fuels in September 2016. Three types of samples were delivered to the participants: peat, wood pellet (not sulphur) and coal. In total 28 participants took part in the PT. Additionally, the participants were asked to estimate or calculate the emission factor for peat and coal samples.

The robust means (or means, n<12) of the results reported by the participants were used as the assigned values for measurements. The uncertainty for the assigned value was estimated at the 95 % confidence interval and it was less than 0.5 % for calorific values and at maximum 10 % for the other measurements.

The evaluation of the performance was based on the z scores, which were calculated using the standard deviation for proficiency assessment at 95 % confidence level. The evaluation of performance was not done for the measurement of M_{ad} in all samples, N in the wood pellet samples and EF in the peat sample. In this proficiency test 90 % of the data was regarded to be satisfactory when the result was accepted to deviate from the assigned value from 1 to 30 %. About 75 % of the participants used the accredited methods and 92 % of their results were satisfactory. In measurements of the gross calorific value from the peat, wood pellet and coal samples, 93 %, 86 % and 84 % of the results were satisfactory, respectively. In measurements of the net calorific value from the peat, wood pellet and coal samples, 82 %, 75 % and 85 % of the results were satisfactory, respectively. In general, the results were in the same range as in the previous similar Proftest SYKE proficiency test in 2015 [6], but the performance in the gross calorific value was somewhat higher and the net calorific value was somewhat lower for peat sample in the present PT.

6 Summary in Finnish

Proftest SYKE järjesti syyskuussa 2016 pätevyyskokeen kalorimetrisen ja tehollisen lämpöarvon sekä tuhkan, vedyn, typen, rikin, kosteuden ja haihtuvien yhdisteiden määrittämiseksi turpeesta, puupelletistä (ei rikkiä) ja kivihiilestä. Lisäksi osallistujilla oli mahdollisuus laskea päästökerroin turve- ja kivihiilinäytteistä.

Pätevyyskokeeseen osallistui yhteensä 28 laboratoriota. Osallistujien pätevyyden arviointi tehtiin z-arvon avulla ja sen laskemisessa käytetyn kokonaishajonnan tavoitearvot olivat määrityksestä riippuen välillä 1–30 %. Mittaussuureen vertailuarvona käytettiin osallistujien ilmoittamien tulosten robustia keskiarvoa tai keskiarvoa, jos tuloksia oli vähän ($n<12$). Tavoitearvon epävarmuus oli lämpöarvomäärityksissä alhaisempi kuin 0,5 % ja muiden määritysten osalta korkeintaan 10 %. Tulosten arviointia ei tehty testinäytteiden kosteuspitoisuuden määritykselle, typen määritykselle puupelletistä eikä päästökertoimen laskennalle turpeesta.

Koko tulosaineistossa hyväksyttäviä tuloksia oli 90 %, kun vertailuarvosta sallittiin 1–30 % poikkeama. Noin 75 % osallistujista käytti akkreditoituja määritysmenetelmiä ja näistä tuloksista oli hyväksyttäviä 92 %. Kalorimetrisen lämpöarvon tuloksista oli hyväksyttäviä 93 % (turve), 86 % (puupelletti) ja 84 % (kivihiili). Tehollisen lämpöarvon tuloksille vastaavat hyväksyttävien tulosten osuudet olivat 82 % (turve), 75 % (puupelletti) ja 85 % (kivihiili). Hyväksyttäviä tuloksia oli lähes saman verran kuin edellisessä vastaavassa pätevyyskokeessa 6/2015 [6], mutta turvenäytteen osalta kalorimetrisen lämpöarvon menestyminen oli parempi ja tehollisen lämpöarvon menestyminen heikompi kuin edellisellä kierroksella.

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APPENDIX 1: Participants in the proficiency test

Country	Institute
Bosnia-Hertsegovina	JP Elektroprivreda d.d.Sarajevo, Z.D. RMU Kakanj d.o.o Kakanj
Bulgary	AES-3C Maritza East 1 EOOD; Testing Laboratory "Energy Materials"
Estonia	Eesti Energia Ölitööstus AS Chemical Laboratory Enefit Energiatootmine AS Tallinn University of Technology, Thermal Engineering Department
Finland	Ahma ympäristö Oy, Oulu BotniaLab Oy Vaasa Ekokem Oy Ab, Riihimäki Finnsementti Oy KCL Kymen Laboratorio Oy Kuopion Energia Oy/ energiantuotanto Kymenlaakson ammattikorkeakoulu Labtium Oy, Jyväskylä Luonnonvarakeskus Kannuksen laboratorio Prosessikemia Ramboll Finland Oy, Vantaa, Industry and Power Plant Chemistry
France	SOCOR Dechy France
Lithuania	Axis Industries Biofuel research Laboratory, Kaunas Cement testing laboratory Co Akmenes cementas
Republic of Ireland	Edenderry Power Ltd
Republic of Korea	Institute of Mine Raclamation Technology, MIRECO Intertek KIMSCO Ulsan Testing Center, South Korea Komipo, Boryeong Thermal Power Site Division The Foundation of Agr. Tech. Commercialization and Transfer
Romania	Air Pollution Laboratory- INCD ECOIND- Bucuresti CRH Ciment (Romania)-Punct de lucru Hoghiz
Sweden	Eurofins Environment testing Sweden AB, Lidköping SP Technical Research Institute of Sweden

APPENDIX 2: Homogeneity of the samples

As the test materials were used in the previous PT CAL 06/2012 [4], the homogeneity was tested from duplicate measurements of two samples per tested sample type. The analytical variation s_{an} and the sampling variation s_{sam} was calculated using one-way variance analysis. For this proficiency test, the analytical results were statistically handled according to the IUPAC guidelines for the treatment of homogeneity testing data and the total standard deviation for proficiency assessment [3, 4].

Criteria for homogeneity:

$s_{an}/s_h<0.5$ and $s_{sam}^2<c$, where

s_h % = standard deviation for testing of homogeneity
s_{an} = analytical deviation, standard deviation of the results within sub samples
s_p% = standard deviation for proficiency assessment
s_{sam} = between-sample deviation, standard deviation of the results between sub samples

$c = F1 \times s_{all}^2 + F2 \times s_a^2$, where
$s_{all}^2 = (0.3 \times s_h)^2$,
F1 and F2 are constants of F distribution derived from the standard statistical tables for the tested number of samples [2, 3].

Table 1. Results from the homogeneity testing of the peat (B1), pellet (B2) and coal (K1) samples.

Measurements	Mean	s_h%	s_p%	s_h	s_{an}	s_{an}/s_h	Is $s_{an}/s_h<0.5$?	s_{sam}	s_{sam}^2	c	Is $s_{sam}^2<c$?
Peat (B1)											
Gross calorific value, J/g	22004	0.3	0.65	66.0	32.4	0.49	yes	26.4	700	10700	yes
Net calorific value, J/g	20721	0.4	0.9	82.9	32.4	0.39	yes	42.7	1821	11600	yes
Pellet (B2)											
Gross calorific value, J/g	20158	0.5	0.75	101	49.0	0.49	yes	0	0	24500	yes
Net calorific value, J/g	18758	0.6	0.9	113	49.0	0.44	yes	0	0	25410	yes
Coal (K1)											
Gross calorific value, J/g	28659	0.2	0.5	57.3	17.0	0.30	yes	0	0	3680	yes
Net calorific value, J/g	27645	0.2	0.6	55.3	17.4	0.32	yes	0	0	3710	yes

Conclusion: In tested cases, the criteria were fulfilled. **Thus, all the samples could be regarded as homogenous.**

APPENDIX 3: Feedback from the proficiency test

FEEDBACK FROM THE PARTICIPANTS

Participant	Comments on technical execution	Action / Proftest
6	The participant appreciated rapidly reported preliminary results.	Proftest SYKE appreciates positive feedback.
8, 14	Participants received the samples within one day after the estimated delivery day.	The used distributor (Posti) did not deliver the samples according to the agreed schedule.
20	The participant informed receiving the samples on 20th September.	According to the distributor's (Posti) tracking system the samples arrived to the participant on 7th September. The provider recommends to check the internal package delivery procedures.
14	The participant informed that the sample size was too small for parallel measurements. The participant informed that they dried sample using their own drying temperature.	Participants can order multiple samples if the informed sample size is not enough for their methods. Own sample drying protocols and temperature are allowed in the test

Participant	Comments to the results	Action / Proftest
17	The participants informed that they reported some results erroneously for coal samples. The corrected results were: Ash: 13.37 w% V_{dp}: 32.35 w% $q_{v,gr,d}$: 28448 J/g S: 0.52	The provider does not correct the results after delivering the preliminary results. The results were handled, when adequate, as outliers in the statistical treatment. All results were satisfactory with the exception of gross calorific value. If it had been reported correctly it would have been satisfactory. The participant can re-calculate the z-scores according to the Guide for participants [5].

FEEDBACK TO THE PARTICIPANTS

Participant	Comments
5	The participants reported only one result instead of replicate results for emission factor in coal (K1) sample. The results have been excluded from the calculation of the assigned values. Also the participants reported emission factor for wood pellet (B2), for which no information for the total moisture contents of the samples as received (M_{ar}) was given. The participants should follow more carefully the instructions given by the provider. Also the participants should check the calculating formula of emission factor.
2, 7, 8, 11, 14, 21, 27	For these participants the deviation of replicate measurements for some measurands and samples were high and their results were Cochran outliers. The provider recommends the participants to validate their deviation of replicate measurements.
All	It was evident, that some uncertainties had been reported erroneously for the measurands (including calorific values), not as relative values as the provider of this proficiency test had requested. Also measurement uncertainty could not be zero as one participants reported. The provider recommends the participants to validate the calculation of measurement uncertainties and follow more carefully the instructions given by the provider.
All	Some of the participants used withdrawn standards as the reference for their measurements. It is recommended that participants should update the reference standards.

APPENDIX 4: Evaluation of the assigned values and their uncertainties

Measurand	Sample	Unit	Assigned value	U_{pt}, %	Evaluation method of assigned value	u_{pt}/s_{pt}
Ash_d	B1	w%	7.11	2.0	Robust mean	0.33
	B2	w%	0.30	9.6	Robust mean	0.32
	K1	w%	13.3	0.5	Robust mean	0.20
C_d	B1	w%	54.4	0.5	Mean	0.17
	B2	w%	50.6	0.4	Mean	0.16
	K1	w%	69.3	0.5	Robust mean	0.20
EF	B1	t CO2/TJ	106	0.4	Mean	
	K1	t CO2/TJ	93.9	1.3	Mean	0.33
H_d	B1	w%	5.62	3.8	Mean	0.54
	B2	w%	6.03	2.3	Mean	0.38
	K1	w%	4.59	1.7	Mean	0.28
$M_{ad,d}$	B1	w%	7.40	4.5	Robust mean	
	B2	w%	7.59	1.7	Robust mean	
	K1	w%	3.79	4.5	Robust mean	
N_d	B1	w%	1.83	2.2	Mean	0.22
	B2	w%	0.07	20.0	Mean	
	K1	w%	2.23	3.2	Mean	0.32
$q_{p,net,d}$	B1	J/g	20768	0.1	Mean	0.06
	B2	J/g	18885	0.2	Mean	0.11
	K1	J/g	27513	0.3	Mean	0.25
$q_{V,gr,d}$	B1	J/g	22035	0.4	Robust mean	0.31
	B2	J/g	20216	0.3	Robust mean	0.20
	K1	J/g	28542	0.3	Robust mean	0.30
S_d	B1	w%	0.20	5.9	Mean	0.30
	K1	w%	0.46	3.2	Robust mean	0.21
V_{db}	B1	w%	66.1	0.5	Mean	0.17
	B2	w%	85.0	0.4	Mean	0.13
	K1	w%	34.8	1.0	Mean	0.33

U_{pt} = Expanded uncertainty of the assigned value
Criterion for reliability of the assigned value $u_{pt}/s_{pt} \leq 0.3$, where
s_{pt}= target value of the standard deviation for proficiency assessment
u_{pt}= standard uncertainty of the assigned value

If $u_{pt}/s_{pt} \leq 0.3$, the assigned value is reliable and the z scores are qualified.

APPENDIX 5: Terms in the results tables

Results of each participant

Measurand	The tested parameter
Sample	The code of the sample
z score	Calculated as follows: $z = (x_i - x_{pt})/s_{pt}$, where x_i = the result of the individual participant x_{pt} = the assigned value s_{pt} = the target value of the standard deviation for proficiency assessment
Assigned value	The value attributed to a particular property of a proficiency test item
2 × s_{pt} %	The target value of total standard deviation for proficiency assessment (s_{pt}) at the 95 % confidence level
Participants's result	The result reported by the participant (the mean value of the replicates)
Md	Median
SD	Standard deviation
SD%	Standard deviation, %
n (stat)	Number of results in statistical processing

Summary on the z scores

S – satisfactory ($-2 \leq z \leq 2$)
Q – questionable ($2 < z < 3$), positive error, the result deviates more than 2 × s_{pt} from the assigned value
q – questionable ($-3 < z < -2$), negative error, the result deviates more than 2 × s_{pt} from the assigned value
U – unsatisfactory ($z \geq 3$), positive error, the result deviates more than 3 × s_{pt} from the assigned value
u – unsatisfactory ($z \leq -3$), negative error, the result deviates more than 3 × s_{pt} from the assigned value

Robust analysis

The items of data are sorted into increasing order, $x_1, x_2, x_i, \ldots, x_p$.
Initial values for x^* and s^* are calculated as:
x^* = median of x_i (i = 1, 2, ...,p)
s^* = 1,483 × median of $|x_i - x^*|$ (i = 1, 2, ...,p)

The mean x^* and s^* are updated as follows:
Calculate $\varphi = 1.5 \times s^*$. A new value is then calculated for each result x_i ($i = 1, 2 \ldots p$):

$$x_i^* = \begin{cases} x^* - \varphi, & \text{if } x_i < x^* - \varphi \\ x^* + \varphi, & \text{if } x_i > x^* + \varphi, \\ x_i & \text{otherwise} \end{cases}$$

The new values of x^* and s^* are calculated from:

$$x^* = \sum x_i^* / p$$

$$s^* = 1.134\sqrt{\sum (x_i^* - x^*)^2 / (p-1)}$$

The robust estimates x^* and s^* can be derived by an iterative calculation, i.e. by updating the values of x^* and s^* several times, until the process convergences [2].

APPENDIX 6: Results of each participant

Participant 1												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		0.87	7.11	6	7.30	7.19	7.11	0.20	2.8	15
	w%	B2		0.53	0.30	30	0.32	0.31	0.30	0.05	15.2	18
	w%	K1		0.93	13.3	2,5	13.5	13.3	13.3	0.2	1.2	19
C_d	w%	B1		-0.50	54.4	3	54.0	54.4	54.4	0.3	0.6	7
	w%	B2		1.85	50.6	2,5	51.8	50.7	50.6	0.3	0.6	10
	w%	K1		-0.50	69.3	2,5	68.9	69.3	69.3	0.4	0.6	14
EF	t CO2/TJ	B1			106		106	106	106	0	0.5	5
	t CO2/TJ	K1		-0.81	93.9	4	92.4	93.2	93.9	1.7	1.8	8
H_d	w%	B1		1.89	5.62	7	5.99	5.65	5.62	0.28	5.0	7
	w%	B2		2.44	6.03	6	6.47	6.03	6.03	0.22	3.7	10
	w%	K1		0.28	4.59	6	4.63	4.61	4.59	0.13	2.9	11
$M_{ad,d}$	w%	B1			7.40		7.32	7.36	7.40	0.41	5.5	12
	w%	B2			7.59		7.68	7.58	7.59	0.11	1.5	17
	w%	K1			3.79		4.12	3.79	3.80	0.23	6.1	18
N_d	w%	B1		0.26	1.83	10	1.85	1.85	1.83	0.05	2.9	7
	w%	B2			0.07		0.09	0.07	0.07	0.02	24.2	6
	w%	K1		0.80	2.23	10	2.32	2.29	2.23	0.11	4.8	9
$q_{p,net,d}$	J/g	B1		0.10	20768	1,7	20786	20784	20768	36	0.2	7
	J/g	B2		0.16	18885	1,8	18913	18906	18885	72	0.4	11
	J/g	K1		0.47	27513	1,2	27591	27571	27513	148	0.5	11
$q_{v,gr,d}$	J/g	B1		0.41	22035	1,3	22094	22037	22034	107	0.5	13
	J/g	B2		0.68	20216	1,5	20320	20220	20216	56	0.3	19
	J/g	K1		0.41	28542	1	28601	28581	28533	124	0.4	17
S_d	w%	B1		0.82	0.20	20	0.22	0.20	0.20	0.02	9.4	10
	w%	K1		1.22	0.46	15	0.50	0.46	0.46	0.02	5.0	17
V_{db}	w%	B1		0.10	66.1	3	66.2	66.1	66.1	0.4	0.7	7
	w%	B2		0.28	85.0	3	85.4	85.0	85.0	0.5	0.6	9
	w%	K1		1.18	34.8	3	35.4	35.0	34.8	0.6	1.8	14

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
C_d	w%	B2		0.21	50.6	2,5	50.7	50.7	50.6	0.3	0.6	10
$M_{ad,d}$	w%	B2			7.59		6.34	7.58	7.59	0.11	1.5	17
$q_{v,gr,d}$	J/g	B2		-7.42	20216	1,5	19091	20220	20216	56	0.3	19

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		0.98	7.11	6	7.32	7.19	7.11	0.20	2.8	15
$M_{ad,d}$	w%	B1			7.40		7.40	7.36	7.40	0.41	5.5	12
$q_{p,net,d}$	J/g	B1		0.03	20768	1,7	20773	20784	20768	36	0.2	7
$q_{v,gr,d}$	J/g	B1		0.01	22035	1,3	22037	22037	22034	107	0.5	13

Participant 4												
Measurand	Unit	Sample	-3 . . 0 . . 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		0.80	7.11	6	7.28	7.19	7.11	0.20	2.8	15
	w%	B2		-1.67	0.30	30	0.23	0.31	0.30	0.05	15.2	18
	w%	K1		-2.35	13.3	2,5	12.9	13.3	13.3	0.2	1.2	19
C_d	w%	B1		-0.39	54.4	3	54.1	54.4	54.4	0.3	0.6	7
	w%	B2		-0.31	50.6	2,5	50.4	50.7	50.6	0.3	0.6	10
	w%	K1		-0.27	69.3	2,5	69.1	69.3	69.3	0.4	0.6	14
EF	t CO2/TJ	B1			106		106	106	106	0	0.5	5
	t CO2/TJ	K1		-0.24	93.9	4	93.5	93.2	93.9	1.7	1.8	8
H_d	w%	B1		1.26	5.62	7	5.87	5.65	5.62	0.28	5.0	7
	w%	B2		-0.41	6.03	6	5.96	6.03	6.03	0.22	3.7	10
	w%	K1		0.78	4.59	6	4.70	4.61	4.59	0.13	2.9	11
$M_{ad,d}$	w%	B1			7.40		6.84	7.36	7.40	0.41	5.5	12
	w%	B2			7.59		7.50	7.58	7.59	0.11	1.5	17
	w%	K1			3.79		3.67	3.79	3.80	0.23	6.1	18
N_d	w%	B1		-0.22	1.83	10	1.81	1.85	1.83	0.05	2.9	7
	w%	B2			0.07		0.06	0.07	0.07	0.02	24.2	6
	w%	K1		0.63	2.23	10	2.30	2.29	2.23	0.11	4.8	9
$q_{p,net,d}$	J/g	B1		-0.35	20768	1,7	20706	20784	20768	36	0.2	7
	J/g	B2		-0.01	18885	1,8	18883	18906	18885	72	0.4	11
	J/g	K1		-0.92	27513	1,2	27362	27571	27513	148	0.5	11
$q_{V,gr,d}$	J/g	B1		-0.40	22035	1,3	21978	22037	22034	107	0.5	13
	J/g	B2		-0.24	20216	1,5	20180	20220	20216	56	0.3	19
	J/g	K1		-1.21	28542	1	28369	28581	28533	124	0.4	17
S_d	w%	B1		1.03	0.20	20	0.22	0.20	0.20	0.02	9.4	10
	w%	K1		-0.23	0.46	15	0.45	0.46	0.46	0.02	5.0	17
V_{db}	w%	B1		0.83	66.1	3	66.9	66.1	66.1	0.4	0.7	7
	w%	B2		0.42	85.0	3	85.5	85.0	85.0	0.5	0.6	9
	w%	K1		0.75	34.8	3	35.2	35.0	34.8	0.6	1.8	14

Participant 5												
Measurand	Unit	Sample	-3 . . 0 . . 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		0.89	7.11	6	7.30	7.19	7.11	0.20	2.8	15
	w%	B2		0.00	0.30	30	0.30	0.31	0.30	0.05	15.2	18
	w%	K1		1.20	13.3	2,5	13.5	13.3	13.3	0.2	1.2	19
C_d	w%	B1		-0.06	54.4	3	54.4	54.4	54.4	0.3	0.6	7
	w%	B2		-0.16	50.6	2,5	50.5	50.7	50.6	0.3	0.6	10
	w%	K1		-0.29	69.3	2,5	69.1	69.3	69.3	0.4	0.6	14
EF	t CO2/TJ	B1			106		95	106	106	0	0.5	5
	t CO2/TJ	K1		-1.04	93.9	4	92.0	93.2	93.9	1.7	1.8	8
H_d	w%	B1		-2.64	5.62	7	5.10	5.65	5.62	0.28	5.0	7
	w%	B2		-2.38	6.03	6	5.60	6.03	6.03	0.22	3.7	10
	w%	K1		-1.38	4.59	6	4.40	4.61	4.59	0.13	2.9	11
$M_{ad,d}$	w%	B1			7.40		7.80	7.36	7.40	0.41	5.5	12
	w%	B2			7.59		7.60	7.58	7.59	0.11	1.5	17
	w%	K1			3.79		3.70	3.79	3.80	0.23	6.1	18
N_d	w%	B1		0.16	1.83	10	1.85	1.85	1.83	0.05	2.9	7
	w%	B2			0.07		*<0,010*	0.07	0.07	0.02	24.2	6
	w%	K1		0.40	2.23	10	2.28	2.29	2.23	0.11	4.8	9

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
$q_{p,net,d}$	J/g	B1		-8.93	20768	1,7	19192	20784	20768	36	0.2	7
	J/g	B2		-9.32	18885	1,8	17302	18906	18885	72	0.4	11
	J/g	K1		-6.62	27513	1,2	26420	27571	27513	148	0.5	11
$q_{v,gr,d}$	J/g	B1		0.75	22035	1,3	22142	22037	22034	107	0.5	13
	J/g	B2		-0.51	20216	1,5	20139	20220	20216	56	0.3	19
	J/g	K1		-0.37	28542	1	28489	28581	28533	124	0.4	17
S_d	w%	B1		0.35	0.20	20	0.21	0.20	0.20	0.02	9.4	10
	w%	K1		0.26	0.46	15	0.47	0.46	0.46	0.02	5.0	17
V_{db}	w%	B1		2.52	66.1	3	68.6	66.1	66.1	0.4	0.7	7
	w%	B2		-0.75	85.0	3	84.1	85.0	85.0	0.5	0.6	9
	w%	K1		1.53	34.8	3	35.6	35.0	34.8	0.6	1.8	14

Participant 6												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	K1		0.18	13.3	2,5	13.3	13.3	13.3	0.2	1.2	19
C_d	w%	K1		0.58	69.3	2,5	69.8	69.3	69.3	0.4	0.6	14
$M_{ad,d}$	w%	K1			3.79		3.78	3.79	3.80	0.23	6.1	18
$q_{v,gr,d}$	J/g	K1		0.29	28542	1	28584	28581	28533	124	0.4	17
S_d	w%	K1		-0.25	0.46	15	0.45	0.46	0.46	0.02	5.0	17
V_{db}	w%	K1		0.17	34.8	3	34.9	35.0	34.8	0.6	1.8	14

Participant 7												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B2		0.00	0.30	30	0.30	0.31	0.30	0.05	15.2	18
	w%	K1		-0.96	13.3	2,5	13.1	13.3	13.3	0.2	1.2	19
C_d	w%	B2		-0.69	50.6	2,5	50.2	50.7	50.6	0.3	0.6	10
	w%	K1		-0.36	69.3	2,5	69.0	69.3	69.3	0.4	0.6	14
EF	t CO2/TJ	K1		1.73	93.9	4	97.1	93.2	93.9	1.7	1.8	8
H_d	w%	B2		-0.32	6.03	6	5.97	6.03	6.03	0.22	3.7	10
	w%	K1		-0.57	4.59	6	4.51	4.61	4.59	0.13	2.9	11
$M_{ad,d}$	w%	B2			7.59		7.59	7.58	7.59	0.11	1.5	17
	w%	K1			3.79		3.44	3.79	3.80	0.23	6.1	18
N_d	w%	B2			0.07		0.08	0.07	0.07	0.02	24.2	6
	w%	K1		0.77	2.23	10	2.32	2.29	2.23	0.11	4.8	9
$q_{p,net,d}$	J/g	B2		-2.52	18885	1,8	18458	18906	18885	72	0.4	11
	J/g	K1		-1.55	27513	1,2	27257	27571	27513	148	0.5	11
$q_{v,gr,d}$	J/g	B2		-3.01	20216	1,5	19760	20220	20216	56	0.3	19
	J/g	K1		-2.21	28542	1	28227	28581	28533	124	0.4	17
S_d	w%	K1		-0.42	0.46	15	0.45	0.46	0.46	0.02	5.0	17

Participant 8												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		-1.45	7.11	6	6.80	7.19	7.11	0.20	2.8	15
	w%	B2		-1.11	0.30	30	0.25	0.31	0.30	0.05	15.2	18
C_d	w%	B1		-5.99	54.4	3	49.5	54.4	54.4	0.3	0.6	7
S_d	w%	B1		1.00	0.20	20	0.22	0.20	0.20	0.02	9.4	10

Participant 9												
Measurand	Unit	Sample	-3 . . 0 . . 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	K1		-0.15	13.3	2,5	13.3	13.3	13.3	0.2	1.2	19
C_d	w%	K1		1.13	69.3	2,5	70.3	69.3	69.3	0.4	0.6	14
EF	t CO2/TJ	K1		0.35	93.9	4	94.6	93.2	93.9	1.7	1.8	8
H_d	w%	K1		-2.50	4.59	6	4.25	4.61	4.59	0.13	2.9	11
$M_{ad,d}$	w%	K1			3.79		3.60	3.79	3.80	0.23	6.1	18
$q_{p,net,d}$	J/g	K1		-0.59	27513	1,2	27415	27571	27513	148	0.5	11
$q_{v,gr,d}$	J/g	K1		-0.50	28542	1	28470	28581	28533	124	0.4	17
S_d	w%	K1		0.62	0.46	15	0.48	0.46	0.46	0.02	5.0	17
V_{db}	w%	K1		1.80	34.8	3	35.7	35.0	34.8	0.6	1.8	14

Participant 10												
Measurand	Unit	Sample	-3 . . 0 . . 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		-0.35	7.11	6	7.04	7.19	7.11	0.20	2.8	15
	w%	B2		-3.78	0.30	30	0.13	0.31	0.30	0.05	15.2	18
$q_{p,net,d}$	J/g	B1		0.19	20768	1,7	20802	20784	20768	36	0.2	7
	J/g	B2		-0.21	18885	1,8	18850	18906	18885	72	0.4	11
$q_{v,gr,d}$	J/g	B1		0.31	22035	1,3	22080	22037	22034	107	0.5	13
	J/g	B2		0.35	20216	1,5	20269	20220	20216	56	0.3	19

Participant 11												
Measurand	Unit	Sample	-3 . . 0 . . 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		-0.28	7.11	6	7.05	7.19	7.11	0.20	2.8	15
	w%	B2		0.22	0.30	30	0.31	0.31	0.30	0.05	15.2	18
	w%	K1		-0.57	13.3	2,5	13.2	13.3	13.3	0.2	1.2	19
C_d	w%	B1		0.03	54.4	3	54.4	54.4	54.4	0.3	0.6	7
	w%	B2		0.32	50.6	2,5	50.8	50.7	50.6	0.3	0.6	10
	w%	K1		-0.54	69.3	2,5	68.8	69.3	69.3	0.4	0.6	14
EF	t CO2/TJ	B1			106		107	106	106	0	0.5	5
	t CO2/TJ	K1		-0.85	93.9	4	92.3	93.2	93.9	1.7	1.8	8
H_d	w%	B1		0.18	5.62	7	5.66	5.65	5.62	0.28	5.0	7
	w%	B2		0.25	6.03	6	6.08	6.03	6.03	0.22	3.7	10
	w%	K1		0.91	4.59	6	4.72	4.61	4.59	0.13	2.9	11
$M_{ad,d}$	w%	B1			7.40		6.88	7.36	7.40	0.41	5.5	12
	w%	B2			7.59		7.48	7.58	7.59	0.11	1.5	17
	w%	K1			3.79		3.87	3.79	3.80	0.23	6.1	18
N_d	w%	B1		-0.12	1.83	10	1.82	1.85	1.83	0.05	2.9	7
	w%	B2			0.07		0.06	0.07	0.07	0.02	24.2	6
	w%	K1		-1.88	2.23	10	2.02	2.29	2.23	0.11	4.8	9
$q_{p,net,d}$	J/g	B1		-0.22	20768	1,7	20729	20784	20768	36	0.2	7
	J/g	B2		0.12	18885	1,8	18906	18906	18885	72	0.4	11
	J/g	K1		0.63	27513	1,2	27617	27571	27513	148	0.5	11
$q_{v,gr,d}$	J/g	B1		-0.57	22035	1,3	21954	22037	22034	107	0.5	13
	J/g	B2		0.09	20216	1,5	20230	20220	20216	56	0.3	19
	J/g	K1		0.59	28542	1	28627	28581	28533	124	0.4	17
S_d	w%	B1		-0.95	0.20	20	0.18	0.20	0.20	0.02	9.4	10
	w%	K1		-0.12	0.46	15	0.46	0.46	0.46	0.02	5.0	17

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		0.68	7.11	6	7.26	7.19	7.11	0.20	2.8	15
	w%	B2		0.78	0.30	30	0.34	0.31	0.30	0.05	15.2	18
$M_{ad,d}$	w%	B1			7.40		6.91	7.36	7.40	0.41	5.5	12
	w%	B2			7.59		6.94	7.58	7.59	0.11	1.5	17
$q_{p,net,d}$	J/g	B1		0.16	20768	1,7	20797	20784	20768	36	0.2	7
	J/g	B2		-0.96	18885	1,8	18722	18906	18885	72	0.4	11
$q_{v,gr,d}$	J/g	B1		-0.12	22035	1,3	22018	22037	22034	107	0.5	13
	J/g	B2		-0.65	20216	1,5	20118	20220	20216	56	0.3	19

Participant 13												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		0.44	7.11	6	7.20	7.19	7.11	0.20	2.8	15
	w%	B2		0.26	0.30	30	0.31	0.31	0.30	0.05	15.2	18
$M_{ad,d}$	w%	B1			7.40		7.88	7.36	7.40	0.41	5.5	12
	w%	B2			7.59		7.79	7.58	7.59	0.11	1.5	17
$q_{p,net,d}$	J/g	B1		0.09	20768	1,7	20784	20784	20768	36	0.2	7
	J/g	B2		0.19	18885	1,8	18918	18906	18885	72	0.4	11
$q_{v,gr,d}$	J/g	B1		-0.21	22035	1,3	22005	22037	22034	107	0.5	13
	J/g	B2		0.03	20216	1,5	20220	20220	20216	56	0.3	19

Participant 14												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B2		0.11	0.30	30	0.31	0.31	0.30	0.05	15.2	18
	w%	K1		0.09	13.3	2,5	13.3	13.3	13.3	0.2	1.2	19
C_d	w%	B2		8.06	50.6	2,5	55.7	50.7	50.6	0.3	0.6	10
	w%	K1		2.51	69.3	2,5	71.5	69.3	69.3	0.4	0.6	14
EF	t CO2/TJ	K1		0.80	93.9	4	95.4	93.2	93.9	1.7	1.8	8
H_d	w%	B2		-3.87	6.03	6	5.33	6.03	6.03	0.22	3.7	10
	w%	K1		-1.80	4.59	6	4.34	4.61	4.59	0.13	2.9	11
$M_{ad,d}$	w%	B2			7.59		8.02	7.58	7.59	0.11	1.5	17
	w%	K1			3.79		5.85	3.79	3.80	0.23	6.1	18
$q_{p,net,d}$	J/g	B2		3.10	18885	1,8	19412	18906	18885	72	0.4	11
	J/g	K1		1.21	27513	1,2	27714	27571	27513	148	0.5	11
$q_{v,gr,d}$	J/g	B2		1.95	20216	1,5	20512	20220	20216	56	0.3	19
	J/g	K1		0.58	28542	1	28625	28581	28533	124	0.4	17
S_d	w%	K1		0.88	0.46	15	0.49	0.46	0.46	0.02	5.0	17

Participant 15												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B2		0.78	0.30	30	0.34	0.31	0.30	0.05	15.2	18
	w%	K1		-0.27	13.3	2,5	13.3	13.3	13.3	0.2	1.2	19
C_d	w%	B2		0.01	50.6	2,5	50.6	50.7	50.6	0.3	0.6	10
	w%	K1		0.32	69.3	2,5	69.6	69.3	69.3	0.4	0.6	14
EF	t CO2/TJ	K1			93.9	4	*92,47*	93.2	93.9	1.7	1.8	8
H_d	w%	B2		-0.83	6.03	6	5.88	6.03	6.03	0.22	3.7	10
	w%	K1		-0.36	4.59	6	4.54	4.61	4.59	0.13	2.9	11
$M_{ad,d}$	w%	B2			7.59		7.49	7.58	7.59	0.11	1.5	17
	w%	K1			3.79		3.87	3.79	3.80	0.23	6.1	18

Participant 15												
Measurand	Unit	Sample	-3 . . 0 . . 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
N_d	w%	B2			0.07		*<0,3*	0.07	0.07	0.02	24.2	6
	w%	K1		-0.94	2.23	10	2.13	2.29	2.23	0.11	4.8	9
$q_{p,net,d}$	J/g	B2		0.55	18885	1,8	18978	18906	18885	72	0.4	11
	J/g	K1		0.35	27513	1,2	27571	27571	27513	148	0.5	11
$q_{V,gr,d}$	J/g	B2		0.28	20216	1,5	20259	20220	20216	56	0.3	19
	J/g	K1		0.00	28542	1	28543	28581	28533	124	0.4	17
S_d	w%	K1		0.58	0.46	15	0.48	0.46	0.46	0.02	5.0	17
V_{db}	w%	B2		-0.41	85.0	3	84.5	85.0	85.0	0.5	0.6	9
	w%	K1		0.47	34.8	3	35.0	35.0	34.8	0.6	1.8	14

Participant 16												
Measurand	Unit	Sample	-3 . . 0 . . 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		-0.47	7.11	6	7.01	7.19	7.11	0.20	2.8	15
	w%	B2		1.89	0.30	30	0.39	0.31	0.30	0.05	15.2	18
	w%	K1		2.23	13.3	2,5	13.7	13.3	13.3	0.2	1.2	19
$q_{p,net,d}$	J/g	B1		-8.56	20768	1,7	19257	20784	20768	36	0.2	7
	J/g	B2		-9.50	18885	1,8	17270	18906	18885	72	0.4	11
	J/g	K1		-5.46	27513	1,2	26612	27571	27513	148	0.5	11
$q_{V,gr,d}$	J/g	B1		-10.89	22035	1,3	20475	22037	22034	107	0.5	13
	J/g	B2		-10.43	20216	1,5	18634	20220	20216	56	0.3	19
	J/g	K1		-7.02	28542	1	27540	28581	28533	124	0.4	17

Participant 17												
Measurand	Unit	Sample	-3 . . 0 . . 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	K1		-1.14	13.3	2,5	13.1	13.3	13.3	0.2	1.2	19
$M_{ad,d}$	w%	K1			3.79		1.94	3.79	3.80	0.23	6.1	18
$q_{V,gr,d}$	J/g	K1		-4.53	28542	1	27896	28581	28533	124	0.4	17
S_d	w%	K1		1.43	0.46	15	0.51	0.46	0.46	0.02	5.0	17
V_{db}	w%	K1		-0.98	34.8	3	34.3	35.0	34.8	0.6	1.8	14

Participant 18												
Measurand	Unit	Sample	-3 . . 0 . . 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B2		1.33	0.30	30	0.36	0.31	0.30	0.05	15.2	18
$M_{ad,d}$	w%	B2			7.59		7.53	7.58	7.59	0.11	1.5	17
$q_{p,net,d}$	J/g	B2		-0.37	18885	1,8	18822	18906	18885	72	0.4	11
$q_{V,gr,d}$	J/g	B2		-0.29	20216	1,5	20172	20220	20216	56	0.3	19

Participant 19												
Measurand	Unit	Sample	-3 . . 0 . . 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	K1		-0.42	13.3	2,5	13.2	13.3	13.3	0.2	1.2	19
C_d	w%	K1		0.24	69.3	2,5	69.5	69.3	69.3	0.4	0.6	14
$M_{ad,d}$	w%	K1			3.79		3.87	3.79	3.80	0.23	6.1	18
$q_{p,net,d}$	J/g	K1		-0.33	27513	1,2	27459	27571	27513	148	0.5	11
$q_{V,gr,d}$	J/g	K1		-0.68	28542	1	28445	28581	28533	124	0.4	17
S_d	w%	K1		0.46	0.46	15	0.48	0.46	0.46	0.02	5.0	17
V_{db}	w%	K1		-1.64	34.8	3	33.9	35.0	34.8	0.6	1.8	14

Participant 20												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	K1		-0.06	13.3	2,5	13.3	13.3	13.3	0.2	1.2	19
$M_{ad,d}$	w%	K1			3.79		3.75	3.79	3.80	0.23	6.1	18
$q_{V,gr,d}$	J/g	K1		0.44	28542	1	28605	28581	28533	124	0.4	17
V_{db}	w%	K1		-2.14	34.8	3	33.7	35.0	34.8	0.6	1.8	14

Participant 21												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		-1.52	7.11	6	6.79	7.19	7.11	0.20	2.8	15
	w%	B2		0.22	0.30	30	0.31	0.31	0.30	0.05	15.2	18
	w%	K1		-0.27	13.3	2,5	13.3	13.3	13.3	0.2	1.2	19
$M_{ad,d}$	w%	B1			7.40		7.18	7.36	7.40	0.41	5.5	12
	w%	B2			7.59		7.51	7.58	7.59	0.11	1.5	17
	w%	K1			3.79		3.81	3.79	3.80	0.23	6.1	18
$q_{V,gr,d}$	J/g	B1		-1.21	22035	1,3	21861	22037	22034	107	0.5	13
	J/g	B2		-0.20	20216	1,5	20186	20220	20216	56	0.3	19
	J/g	K1		0.23	28542	1	28575	28581	28533	124	0.4	17
S_d	w%	B1		-1.50	0.20	20	0.17	0.20	0.20	0.02	9.4	10
	w%	K1		-0.29	0.46	15	0.45	0.46	0.46	0.02	5.0	17
V_{db}	w%	B1		-0.03	66.1	3	66.1	66.1	66.1	0.4	0.7	7
	w%	B2		-3.40	85.0	3	80.7	85.0	85.0	0.5	0.6	9
	w%	K1		-6.02	34.8	3	31.7	35.0	34.8	0.6	1.8	14

Participant 22												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		0.38	7.11	6	7.19	7.19	7.11	0.20	2.8	15
	w%	B2		-1.56	0.30	30	0.23	0.31	0.30	0.05	15.2	18
	w%	K1		0.09	13.3	2,5	13.3	13.3	13.3	0.2	1.2	19
C_d	w%	B1		0.58	54.4	3	54.9	54.4	54.4	0.3	0.6	7
	w%	B2		0.42	50.6	2,5	50.9	50.7	50.6	0.3	0.6	10
	w%	K1		-0.03	69.3	2,5	69.3	69.3	69.3	0.4	0.6	14
EF	t CO2/TJ	B1			106		106	106	106	0	0.5	5
	t CO2/TJ	K1		-0.64	93.9	4	92.7	93.2	93.9	1.7	1.8	8
H_d	w%	B1		-0.27	5.62	7	5.57	5.65	5.62	0.28	5.0	7
	w%	B2		0.02	6.03	6	6.03	6.03	6.03	0.22	3.7	10
	w%	K1		0.52	4.59	6	4.66	4.61	4.59	0.13	2.9	11
$M_{ad,d}$	w%	B1			7.40		7.49	7.36	7.40	0.41	5.5	12
	w%	B2			7.59		7.71	7.58	7.59	0.11	1.5	17
	w%	K1			3.79		4.32	3.79	3.80	0.23	6.1	18
N_d	w%	B1		0.31	1.83	10	1.86	1.85	1.83	0.05	2.9	7
	w%	B2			0.07		0.09	0.07	0.07	0.02	24.2	6
	w%	K1		0.69	2.23	10	2.31	2.29	2.23	0.11	4.8	9
$q_{p,net,d}$	J/g	B1		1.27	20768	1,7	20992	20784	20768	36	0.2	7
	J/g	B2		0.52	18885	1,8	18973	18906	18885	72	0.4	11
	J/g	K1		0.88	27513	1,2	27659	27571	27513	148	0.5	11
$q_{V,gr,d}$	J/g	B1		1.14	22035	1,3	22199	22037	22034	107	0.5	13
	J/g	B2		0.47	20216	1,5	20288	20220	20216	56	0.3	19
	J/g	K1		0.82	28542	1	28659	28581	28533	124	0.4	17
S_d	w%	B1		-0.45	0.20	20	0.19	0.20	0.20	0.02	9.4	10

Participant 22												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
S_d	w%	K1		-0.62	0.46	15	0.44	0.46	0.46	0.02	5.0	17
V_{db}	w%	B1		-0.57	66.1	3	65.5	66.1	66.1	0.4	0.7	7
	w%	B2		-0.02	85.0	3	85.0	85.0	85.0	0.5	0.6	9
	w%	K1		-0.96	34.8	3	34.3	35.0	34.8	0.6	1.8	14

Participant 23												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
$q_{V,gr,d}$	J/g	B2		0.04	20216	1,5	20223	20220	20216	56	0.3	19

Participant 24												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B2		0.44	0.30	30	0.32	0.31	0.30	0.05	15.2	18
	w%	K1		-0.30	13.3	2,5	13.3	13.3	13.3	0.2	1.2	19
C_d	w%	B2		-0.85	50.6	2,5	50.1	50.7	50.6	0.3	0.6	10
	w%	K1		-0.60	69.3	2,5	68.8	69.3	69.3	0.4	0.6	14
H_d	w%	B2		0.47	6.03	6	6.11	6.03	6.03	0.22	3.7	10
	w%	K1		0.16	4.59	6	4.61	4.61	4.59	0.13	2.9	11
$M_{ad,d}$	w%	B2			7.59		7.49	7.58	7.59	0.11	1.5	17
	w%	K1			3.79		3.66	3.79	3.80	0.23	6.1	18
N_d	w%	B2			0.07		0.20	0.07	0.07	0.02	24.2	6
	w%	K1		4.51	2.23	10	2.73	2.29	2.23	0.11	4.8	9
$q_{p,net,d}$	J/g	B2		-0.16	18885	1,8	18859	18906	18885	72	0.4	11
	J/g	K1		-0.91	27513	1,2	27363	27571	27513	148	0.5	11
$q_{V,gr,d}$	J/g	B2		-0.16	20216	1,5	20191	20220	20216	56	0.3	19
	J/g	K1		-1.34	28542	1	28351	28581	28533	124	0.4	17
S_d	w%	K1		-1.07	0.46	15	0.42	0.46	0.46	0.02	5.0	17
V_{db}	w%	B2		0.40	85.0	3	85.5	85.0	85.0	0.5	0.6	9
	w%	K1		1.43	34.8	3	35.5	35.0	34.8	0.6	1.8	14

Participant 25												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		0.77	7.11	6	7.28	7.19	7.11	0.20	2.8	15
	w%	B2		-0.47	0.30	30	0.28	0.31	0.30	0.05	15.2	18
	w%	K1		-0.35	13.3	2,5	13.2	13.3	13.3	0.2	1.2	19
C_d	w%	B1		0.52	54.4	3	54.8	54.4	54.4	0.3	0.6	7
	w%	B2		0.20	50.6	2,5	50.7	50.7	50.6	0.3	0.6	10
	w%	K1		0.06	69.3	2,5	69.4	69.3	69.3	0.4	0.6	14
EF	t CO2/TJ	B1			106		107	106	106	0	0.5	5
	t CO2/TJ	K1		-0.48	93.9	4	93.0	93.2	93.9	1.7	1.8	8
H_d	w%	B1		0.14	5.62	7	5.65	5.65	5.62	0.28	5.0	7
	w%	B2		0.95	6.03	6	6.20	6.03	6.03	0.22	3.7	10
	w%	K1		1.38	4.59	6	4.78	4.61	4.59	0.13	2.9	11
$M_{ad,d}$	w%	B1			7.40		7.86	7.36	7.40	0.41	5.5	12
	w%	B2			7.59		7.78	7.58	7.59	0.11	1.5	17
	w%	K1			3.79		3.86	3.79	3.80	0.23	6.1	18
N_d	w%	B1		0.60	1.83	10	1.89	1.85	1.83	0.05	2.9	7
	w%	B2			0.07		0.05	0.07	0.07	0.02	24.2	6
	w%	K1		0.54	2.23	10	2.29	2.29	2.23	0.11	4.8	9

Participant 25												
Measurand	Unit	Sample	-3 . . 0 . . 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
$q_{p,net,d}$	J/g	B1		0.52	20768	1,7	20861	20784	20768	36	0.2	7
	J/g	B2		0.16	18885	1,8	18913	18906	18885	72	0.4	11
	J/g	K1		0.73	27513	1,2	27633	27571	27513	148	0.5	11
$q_{v,gr,d}$	J/g	B1		0.28	22035	1,3	22075	22037	22034	107	0.5	13
	J/g	B2		0.31	20216	1,5	20263	20220	20216	56	0.3	19
	J/g	K1		0.83	28542	1	28661	28581	28533	124	0.4	17
S_d	w%	B1		-0.19	0.20	20	0.20	0.20	0.20	0.02	9.4	10
	w%	K1		-0.28	0.46	15	0.45	0.46	0.46	0.02	5.0	17
V_{db}	w%	B1		-0.32	66.1	3	65.8	66.1	66.1	0.4	0.7	7
	w%	B2		-0.36	85.0	3	84.5	85.0	85.0	0.5	0.6	9
	w%	K1		-0.11	34.8	3	34.7	35.0	34.8	0.6	1.8	14

Participant 26												
Measurand	Unit	Sample	-3 . . 0 . . 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		-1.71	7.11	6	6.75	7.19	7.11	0.20	2.8	15
	w%	B2		0.44	0.30	30	0.32	0.31	0.30	0.05	15.2	18
	w%	K1		-0.78	13.3	2,5	13.2	13.3	13.3	0.2	1.2	19
C_d	w%	B1		0.07	54.4	3	54.5	54.4	54.4	0.3	0.6	7
	w%	B2		0.36	50.6	2,5	50.8	50.7	50.6	0.3	0.6	10
	w%	K1		0.19	69.3	2,5	69.5	69.3	69.3	0.4	0.6	14
H_d	w%	B1		-0.43	5.62	7	5.54	5.65	5.62	0.28	5.0	7
	w%	B2		0.00	6.03	6	6.03	6.03	6.03	0.22	3.7	10
	w%	K1		-0.11	4.59	6	4.58	4.61	4.59	0.13	2.9	11
$M_{ad,d}$	w%	B1			7.40		7.27	7.36	7.40	0.41	5.5	12
	w%	B2			7.59		7.58	7.58	7.59	0.11	1.5	17
	w%	K1			3.79		4.03	3.79	3.80	0.23	6.1	18
N_d	w%	B1		-1.20	1.83	10	1.72	1.85	1.83	0.05	2.9	7
	w%	B2			0.07		0.17	0.07	0.07	0.02	24.2	6
	w%	K1		-0.63	2.23	10	2.16	2.29	2.23	0.11	4.8	9
$q_{v,gr,d}$	J/g	B1		0.84	22035	1,3	22156	22037	22034	107	0.5	13
	J/g	B2		1.95	20216	1,5	20512	20220	20216	56	0.3	19
	J/g	K1		0.75	28542	1	28649	28581	28533	124	0.4	17
S_d	w%	B1		-1.25	0.20	20	0.18	0.20	0.20	0.02	9.4	10
	w%	K1		-0.14	0.46	15	0.46	0.46	0.46	0.02	5.0	17
V_{db}	w%	B1		-0.34	66.1	3	65.8	66.1	66.1	0.4	0.7	7
	w%	B2		-0.24	85.0	3	84.7	85.0	85.0	0.5	0.6	9
	w%	K1		-0.72	34.8	3	34.4	35.0	34.8	0.6	1.8	14

Participant 27												
Measurand	Unit	Sample	-3 . . 0 . . 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		-0.30	7.11	6	7.05	7.19	7.11	0.20	2.8	15
	w%	B2		-1.89	0.30	30	0.22	0.31	0.30	0.05	15.2	18
	w%	K1		0.48	13.3	2,5	13.4	13.3	13.3	0.2	1.2	19
$M_{ad,d}$	w%	B1			7.40		7.95	7.36	7.40	0.41	5.5	12
	w%	B2			7.59		8.27	7.58	7.59	0.11	1.5	17
	w%	K1			3.79		3.42	3.79	3.80	0.23	6.1	18
$q_{v,gr,d}$	J/g	B1		-1.34	22035	1,3	21843	22037	22034	107	0.5	13
	J/g	B2		-0.24	20216	1,5	20180	20220	20216	56	0.3	19

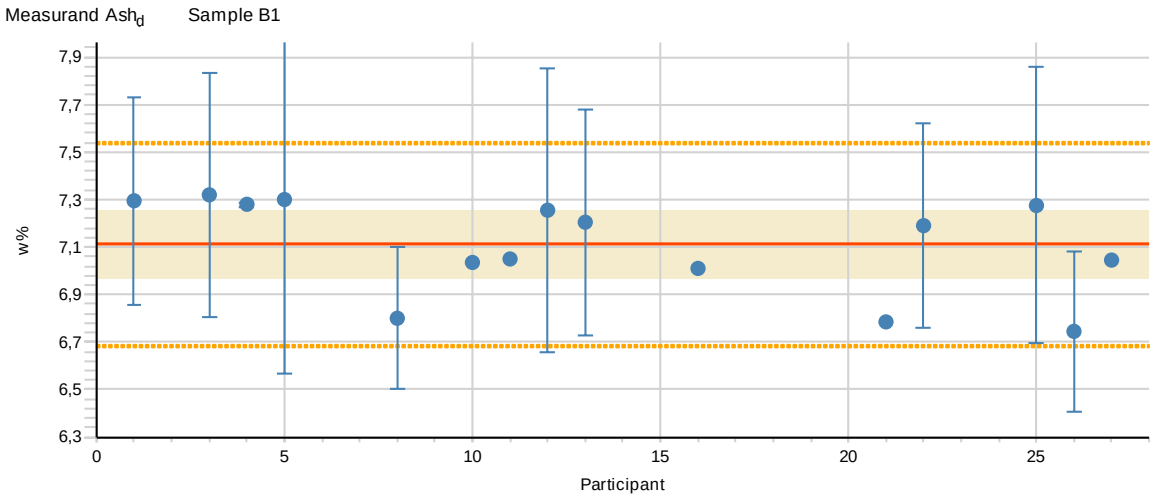
Participant 27												
Measurand	Unit	Sample	-3 . . 0 . . 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
$q_{V,gr,d}$	J/g	K1		0.27	28542	1	28581	28581	28533	124	0.4	17
S_d	w%	B1		0.30	0.20	20	0.21	0.20	0.20	0.02	9.4	10
	w%	K1		0.39	0.46	15	0.47	0.46	0.46	0.02	5.0	17
V_{db}	w%	B1		0.05	66.1	3	66.1	66.1	66.1	0.4	0.7	7
	w%	B2		0.33	85.0	3	85.4	85.0	85.0	0.5	0.6	9
	w%	K1		0.54	34.8	3	35.1	35.0	34.8	0.6	1.8	14

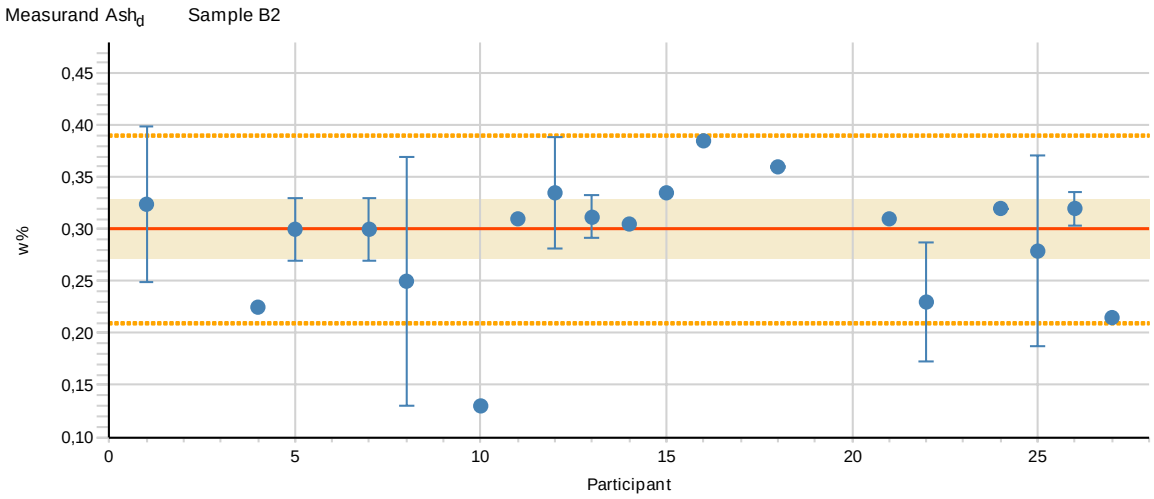
Participant 28												
Measurand	Unit	Sample	-3 . . 0 . . 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
$q_{p,net,d}$	J/g	B2		0.03	18885	1,8	18891	18906	18885	72	0.4	11
$q_{V,gr,d}$	J/g	B2		0.06	20216	1,5	20225	20220	20216	56	0.3	19

APPENDIX 7: Results of participants and their uncertainties

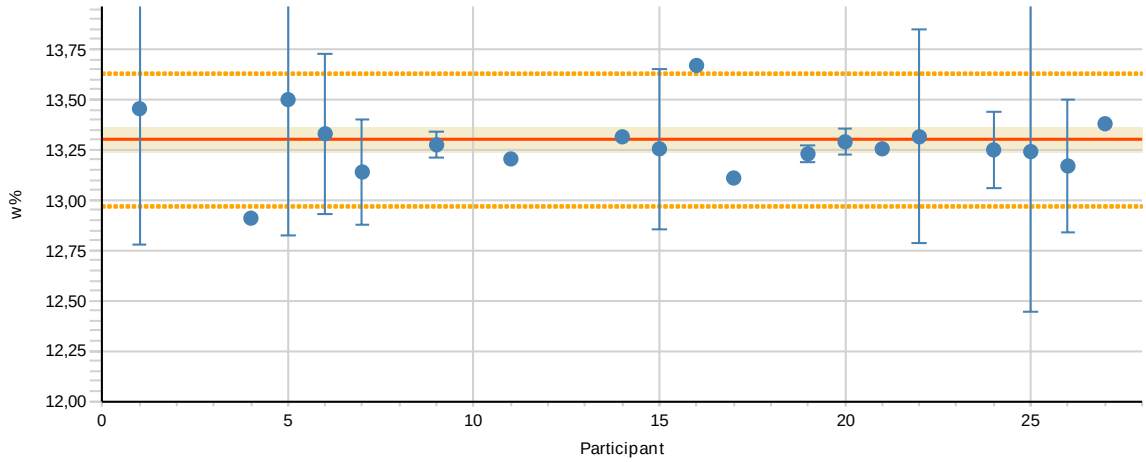
In figures:

- The dashed lines describe the standard deviation for the proficiency assessment, the red solid line shows the assigned value, the shaded area describes the expanded measurement uncertainty of the assigned value, and the arrow describes the value outside the scale.

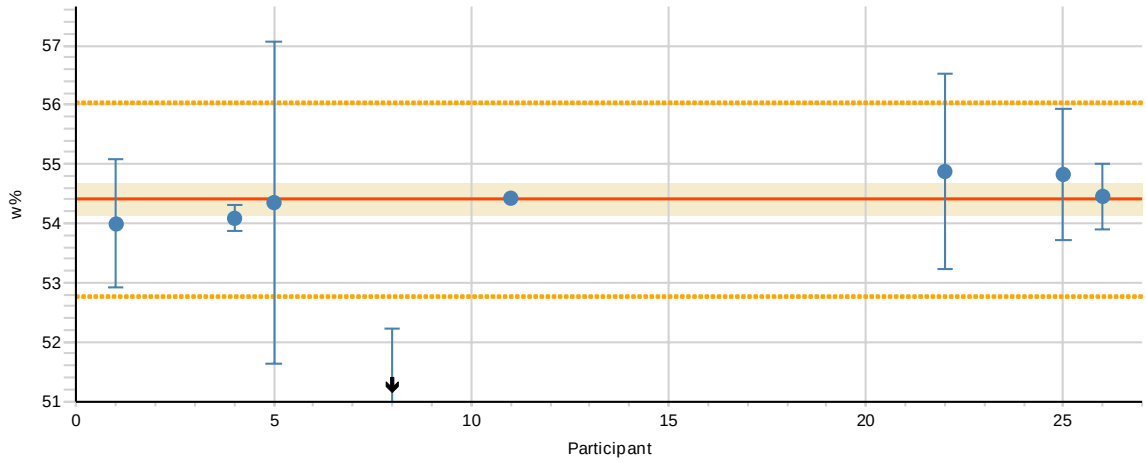




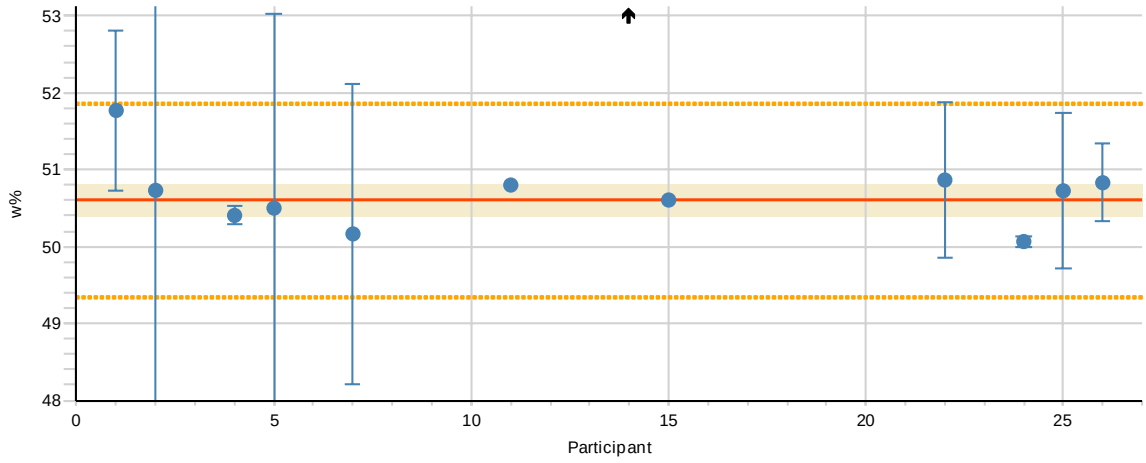
Measurand Ash_d Sample K1



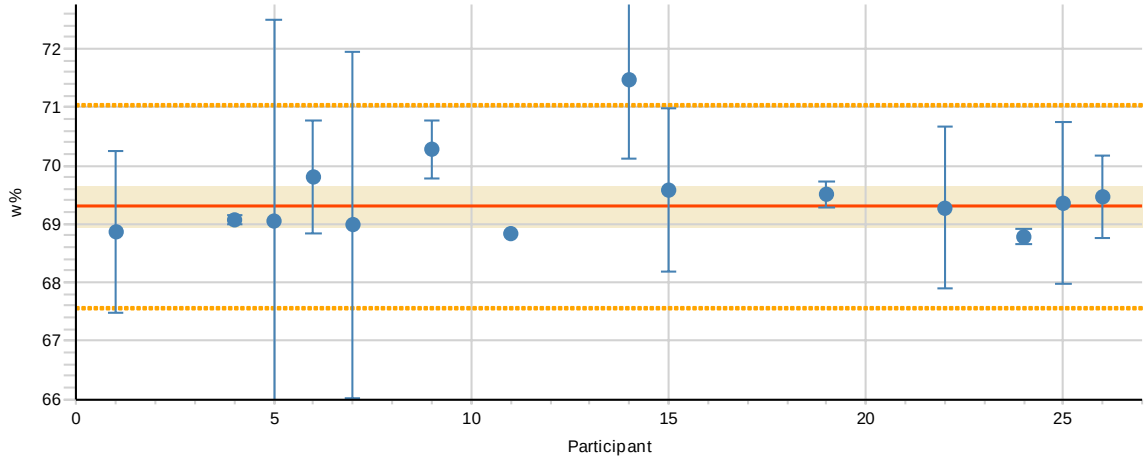
Measurand C_d Sample B1



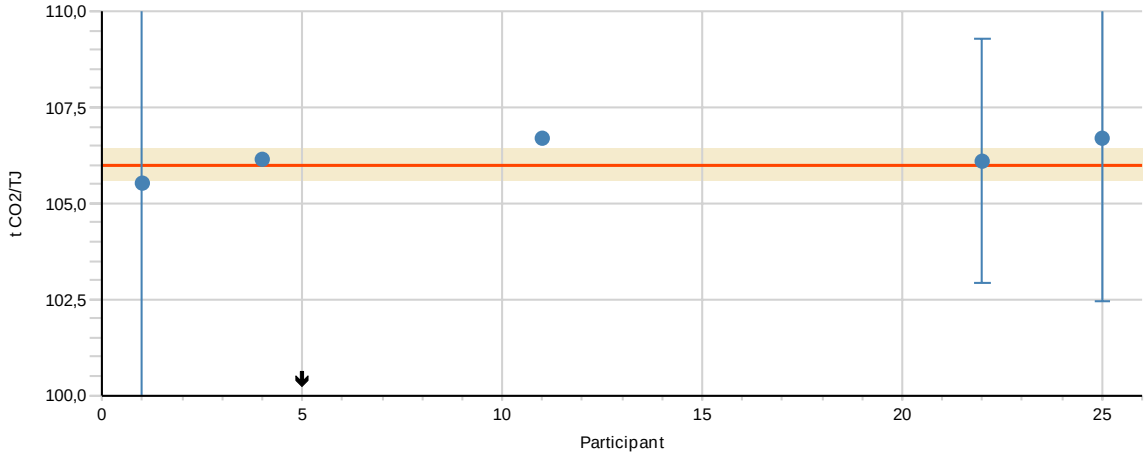
Measurand C_d Sample B2



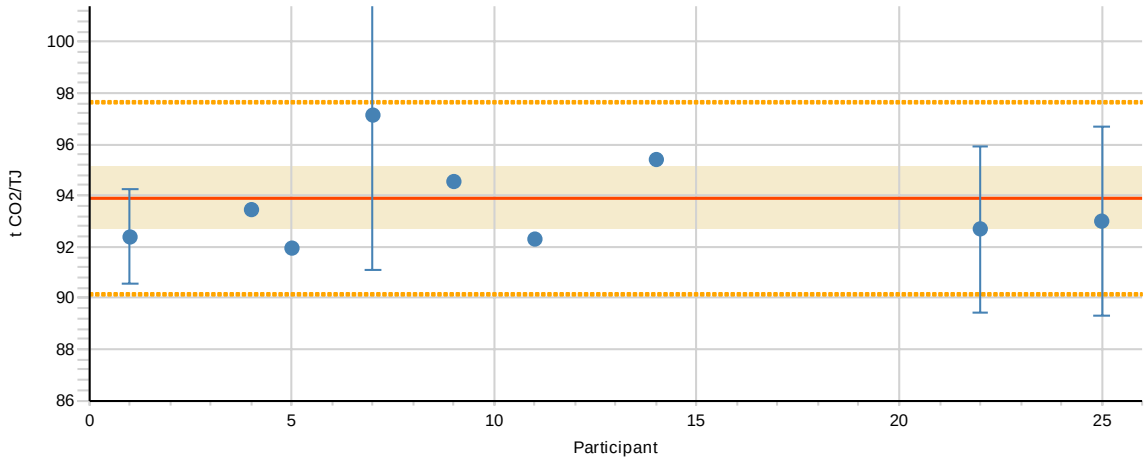
Measurand C_d Sample K1



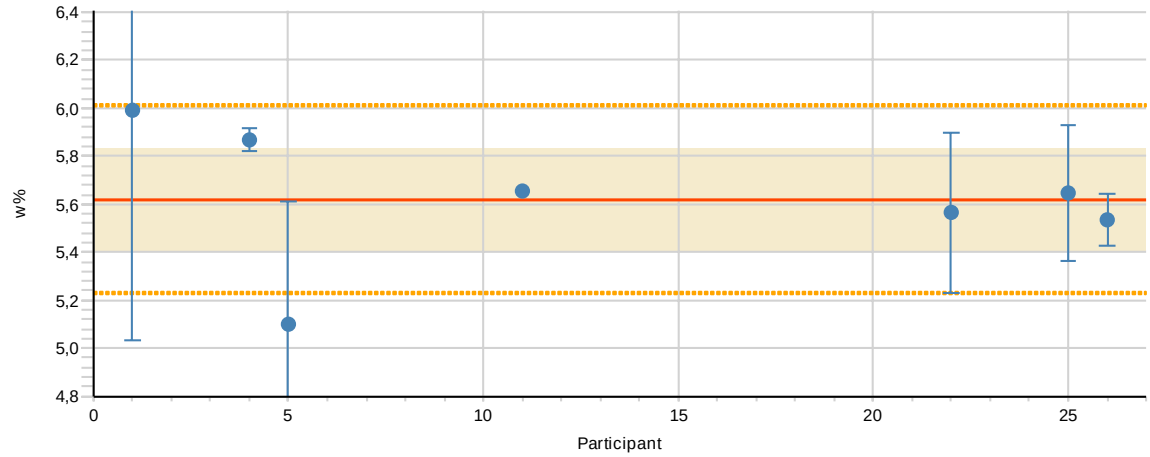
Measurand EF Sample B1



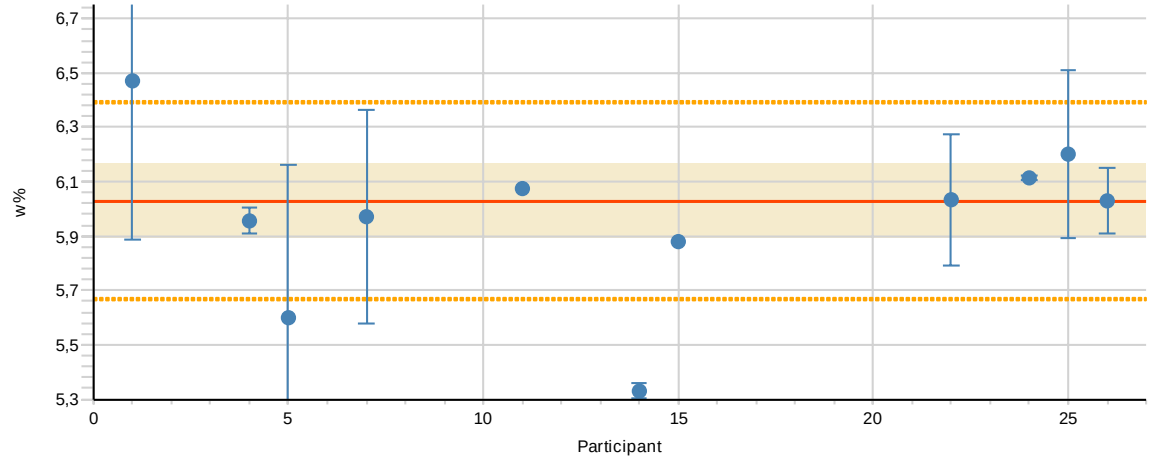
Measurand EF Sample K1



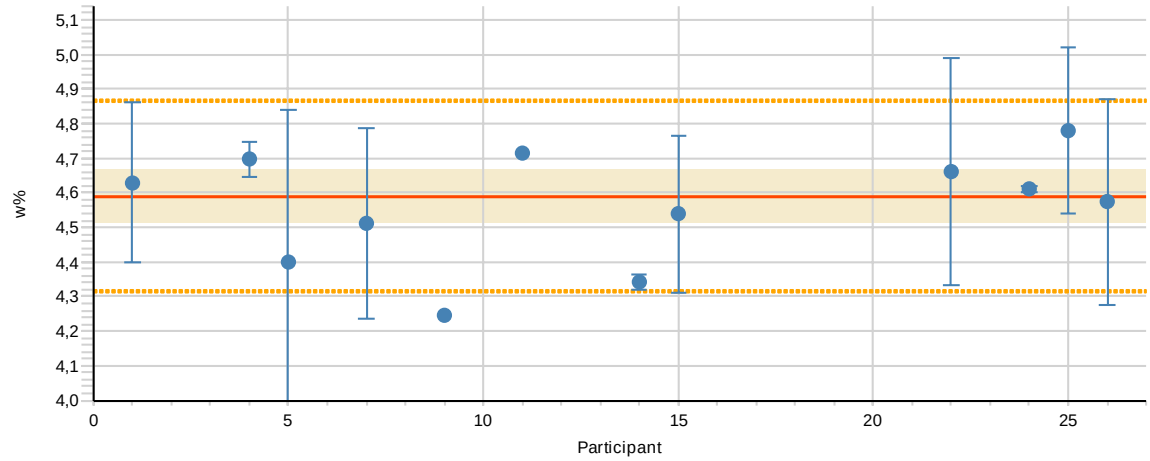
Measurand H_d Sample B1



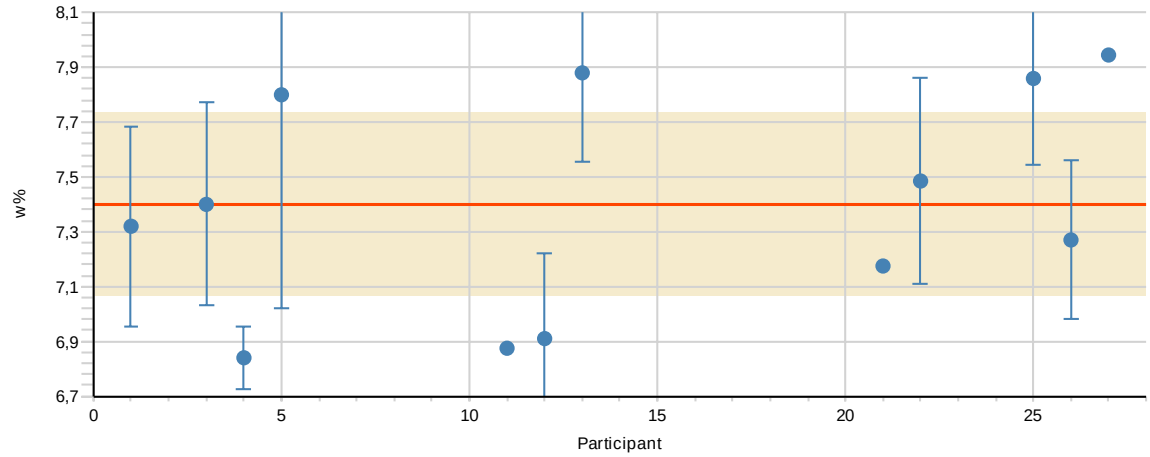
Measurand H_d Sample B2



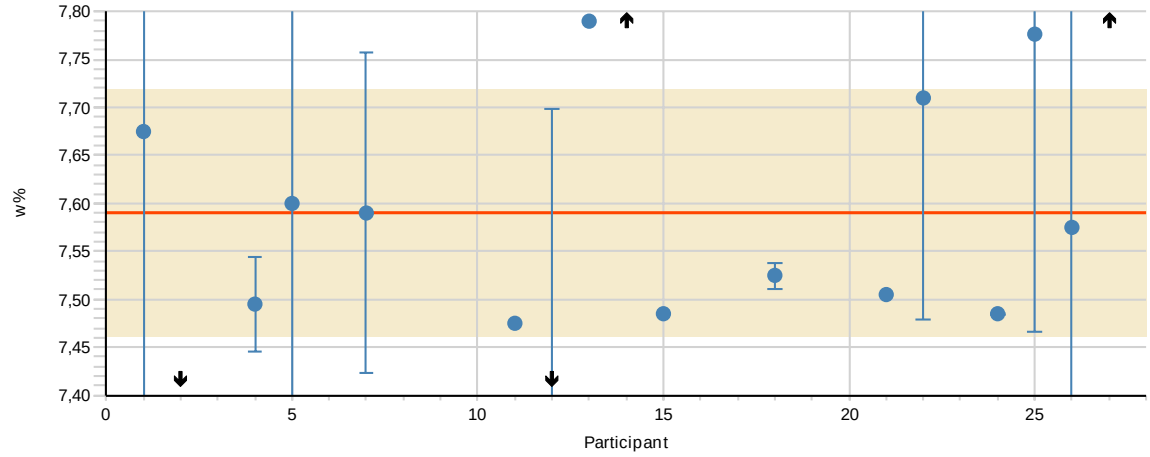
Measurand H_d Sample K1



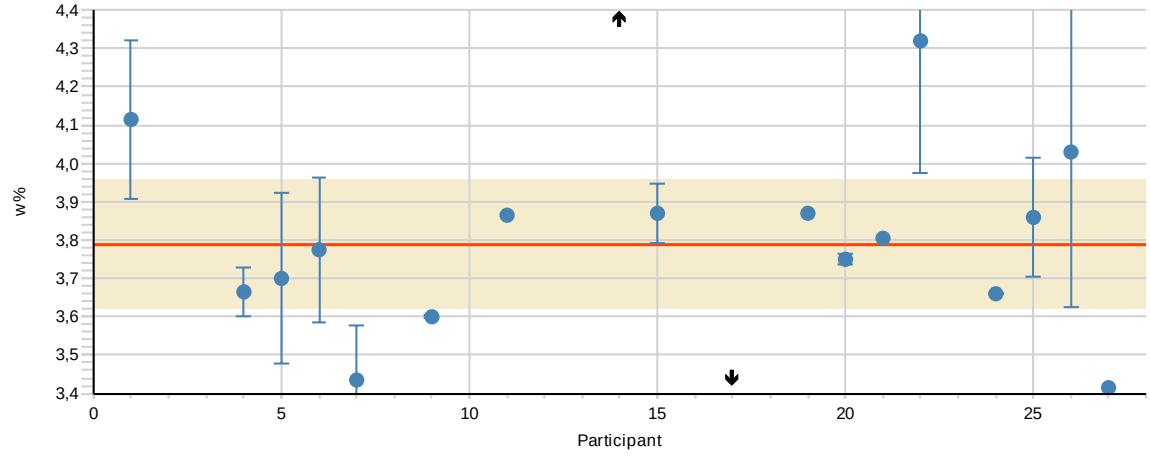
Measurand $M_{ad, d}$ Sample B1

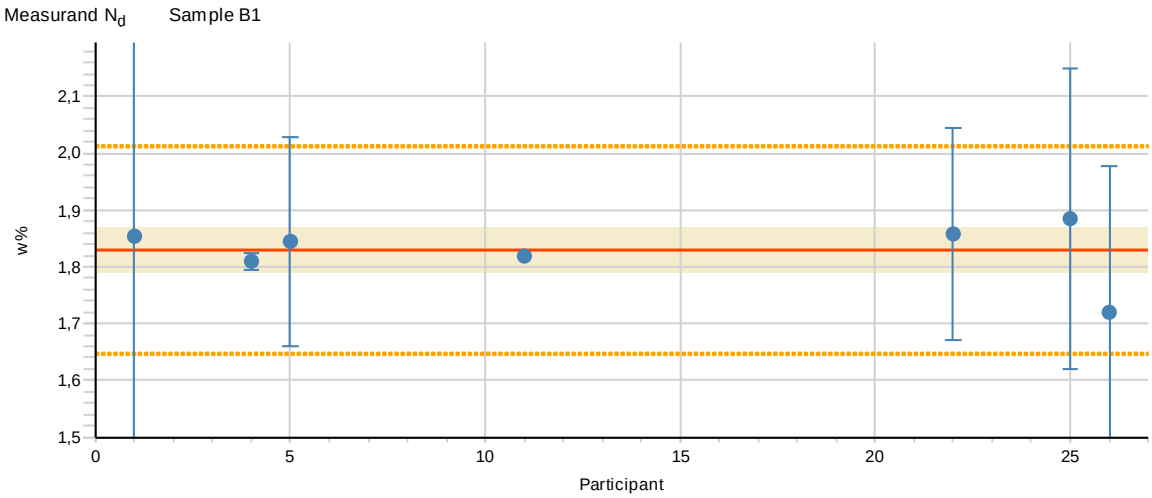


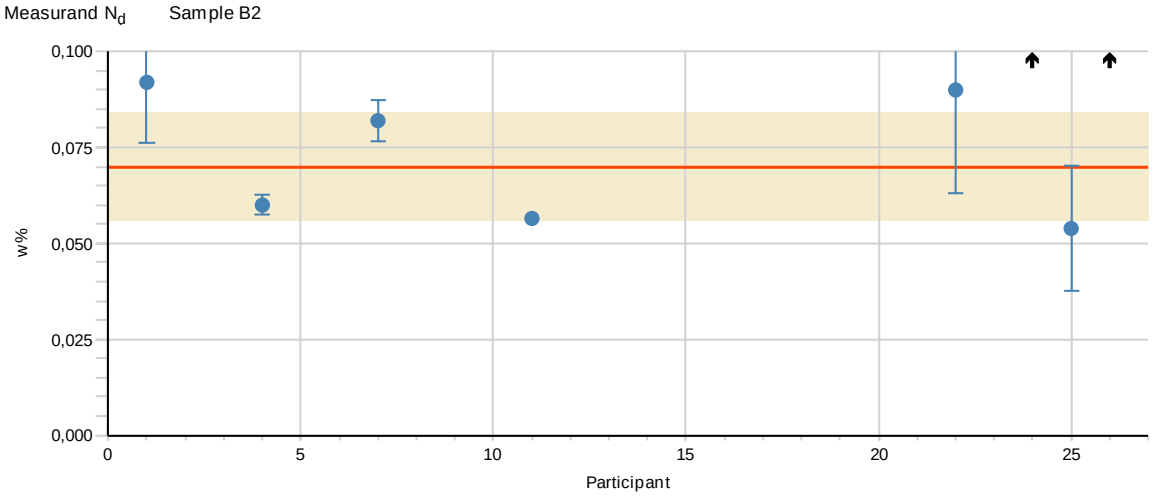
Measurand $M_{ad, d}$ Sample B2

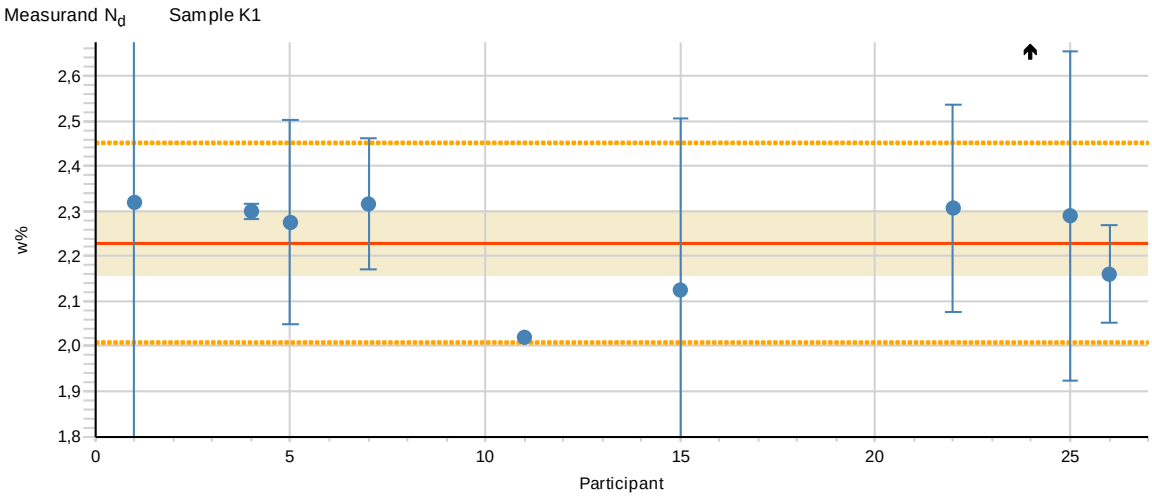


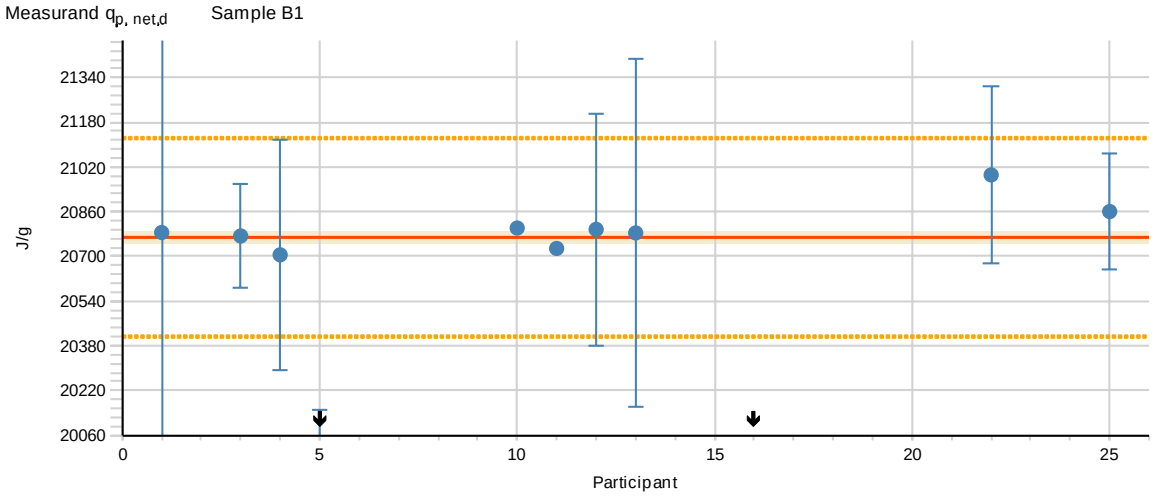
Measurand $M_{ad, d}$ Sample K1

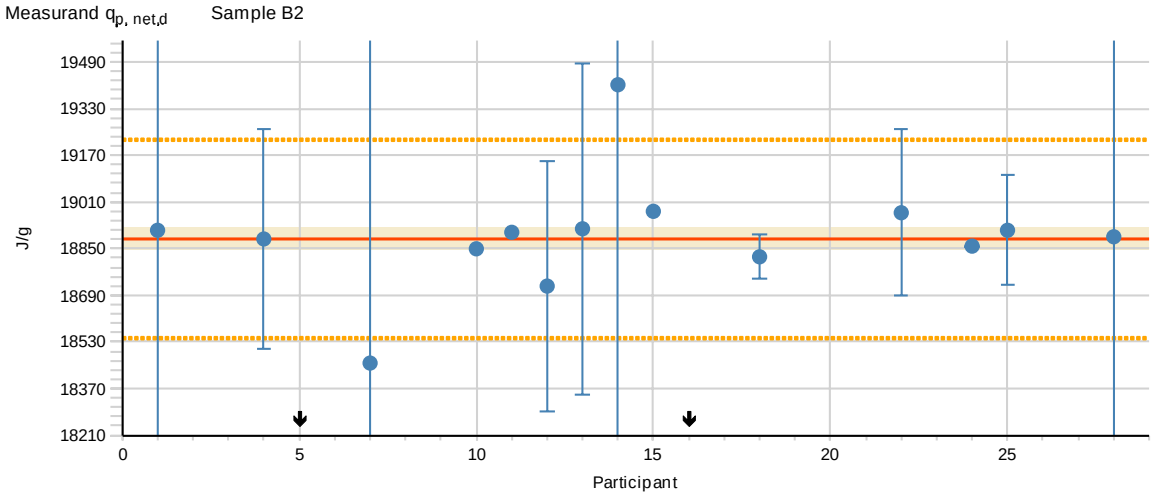


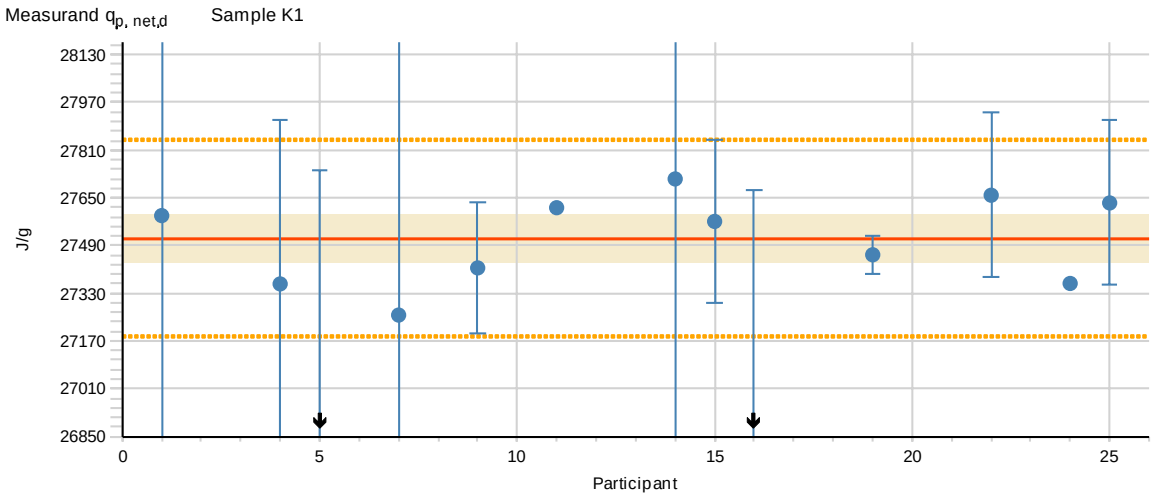

Measurand N_d
Sample B1
w%
2,1
2,0
1,9
1,8
1,7
1,6
1,5
0
5
10
15
20
25
Participant

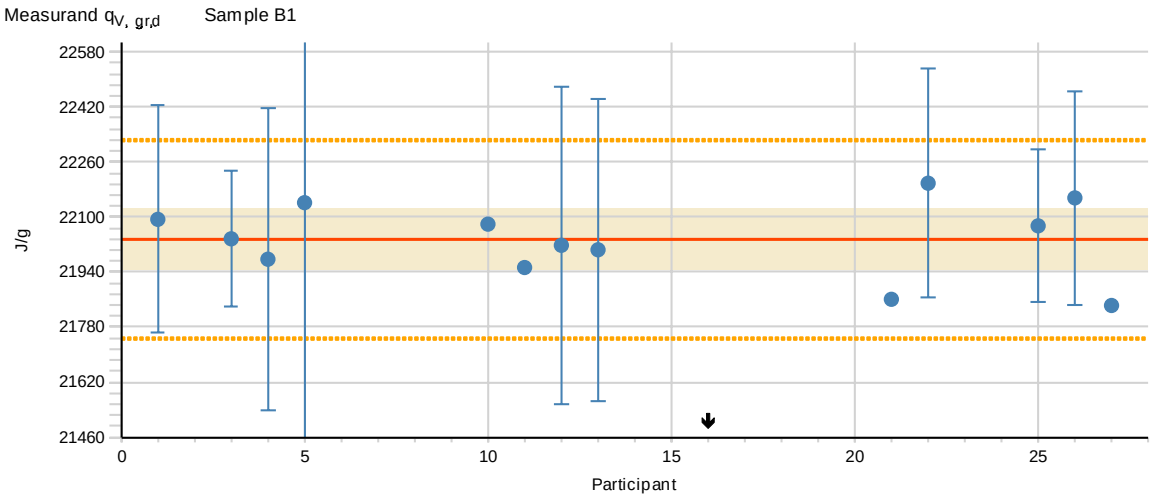

Measurand N_d
Sample B2
w%
0,100
0,075
0,050
0,025
0,000
0
5
10
15
20
25
Participant

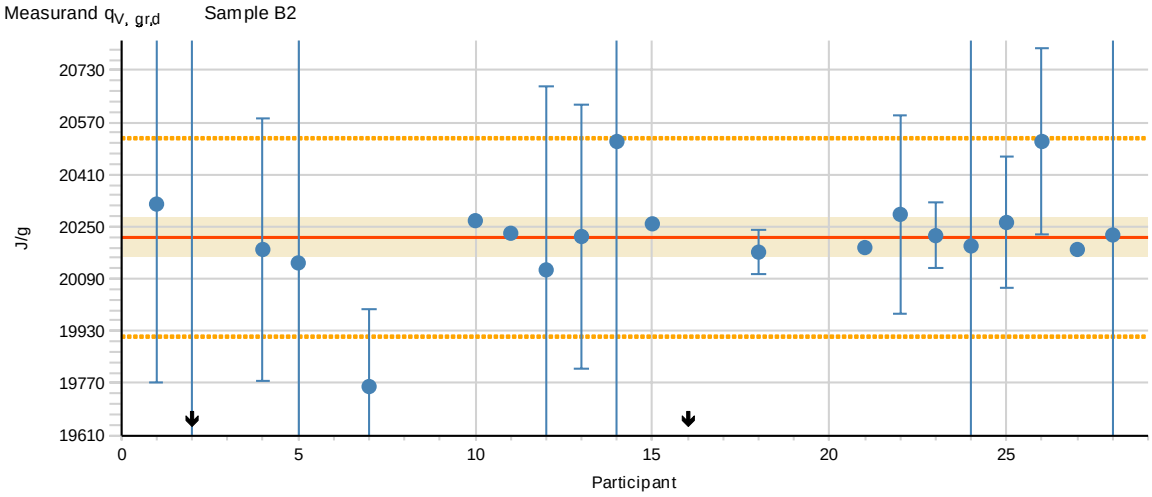

Measurand N_d
Sample K1
w%
2,6
2,5
2,4
2,3
2,2
2,1
2,0
1,9
1,8
0
5
10
15
20
25
Participant

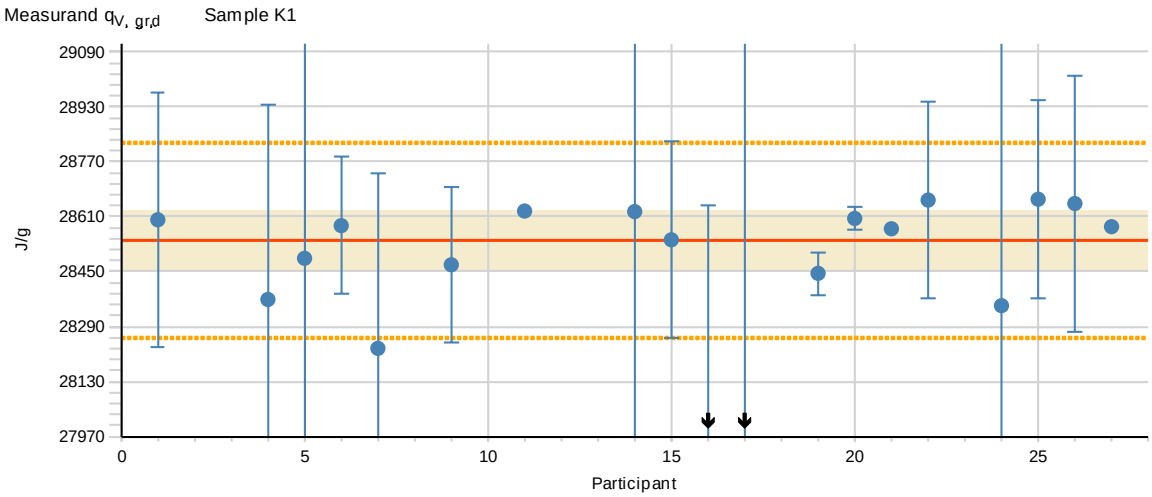

Measurand $q_{p,\,net,d}$
Sample B1
J/g
21340
21180
21020
20860
20700
20540
20380
20220
20060
0
5
10
15
20
25
Participant


Measurand $q_{p,\,net,d}$
Sample B2
J/g
19490
19330
19170
19010
18850
18690
18530
18370
18210
0
5
10
15
20
25
Participant

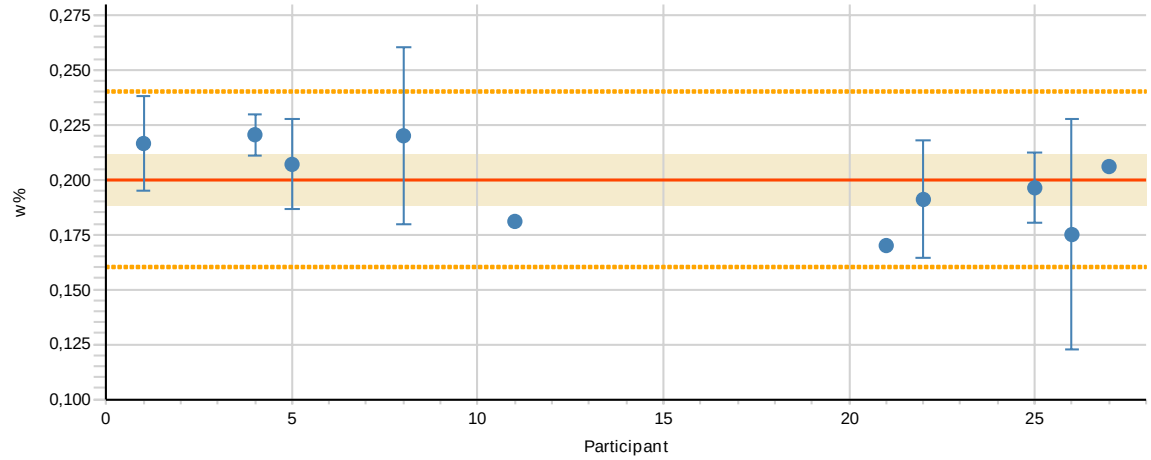

Measurand $q_{p,\,net,d}$
Sample K1
J/g
28130
27970
27810
27650
27490
27330
27170
27010
26850
0
5
10
15
20
25
Participant


Measurand $q_{V,\,gr,d}$
Sample B1
22580
22420
22260
22100
21940
21780
21620
21460
J/g
0
5
10
15
20
25
Participant

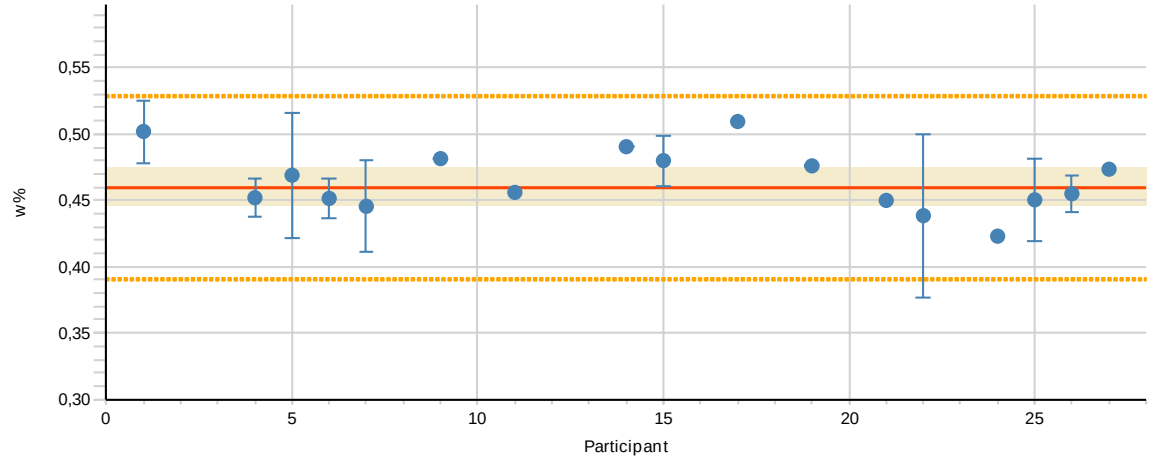

Measurand $q_{V,\,gr,d}$
Sample B2
20730
20570
20410
20250
20090
19930
19770
19610
J/g
0
5
10
15
20
25
Participant


Measurand $q_{V,\,gr,d}$
Sample K1
29090
28930
28770
28610
28450
28290
28130
27970
J/g
0
5
10
15
20
25
Participant

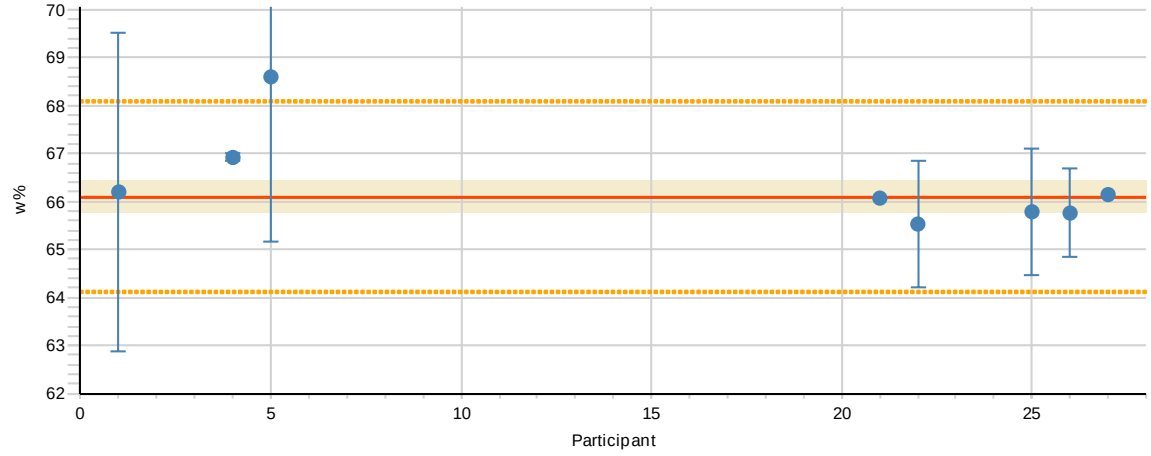
Measurand S_d Sample B1

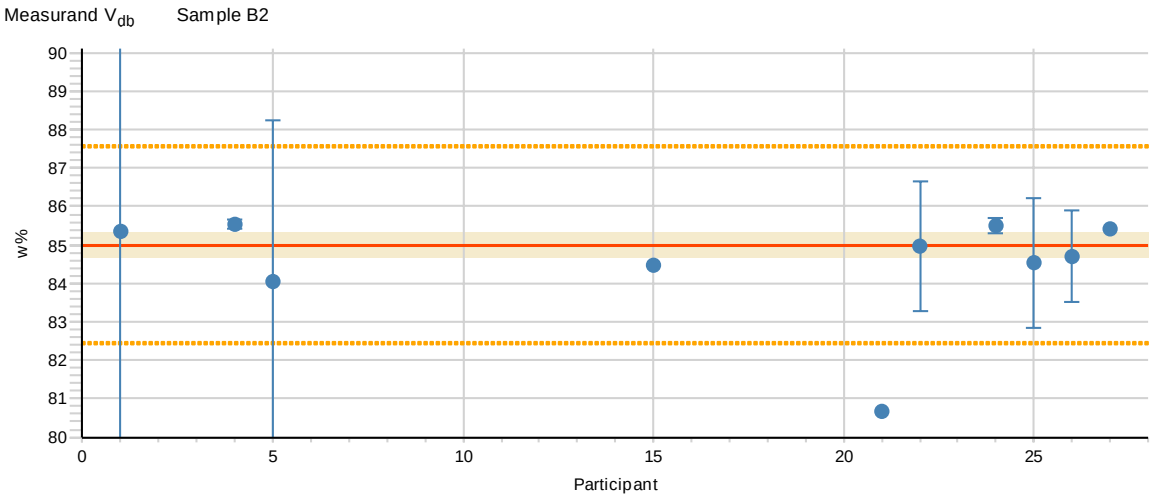


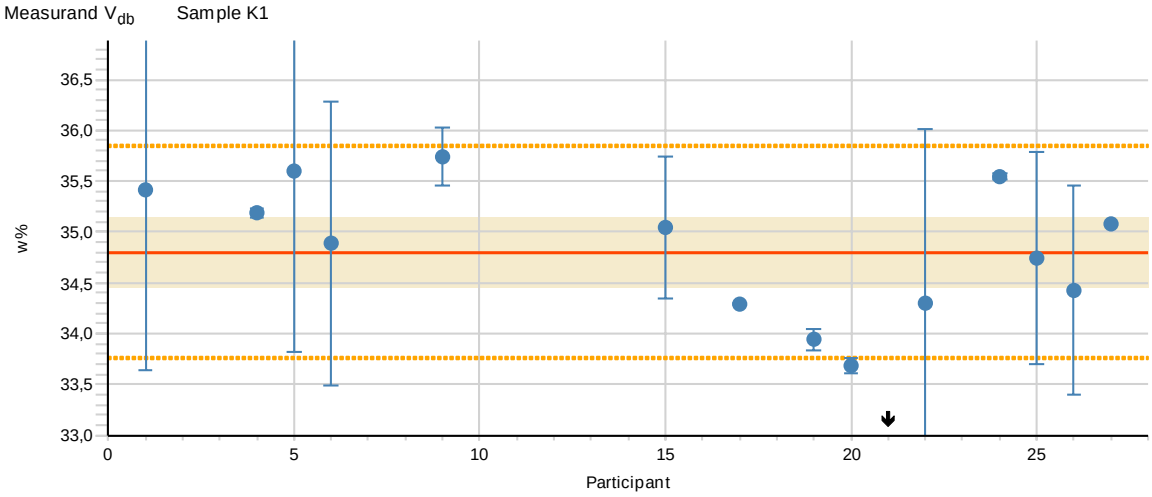
Measurand S_d Sample K1



Measurand V_{db} Sample B1




Measurand V_{db}
Sample B2
w%
90
89
88
87
86
85
84
83
82
81
80
0
5
10
15
20
25
Participant


Measurand V_{db}
Sample K1
w%
36,5
36,0
35,5
35,0
34,5
34,0
33,5
33,0
0
5
10
15
20
25
Participant

APPENDIX 8: Summary of the z scores

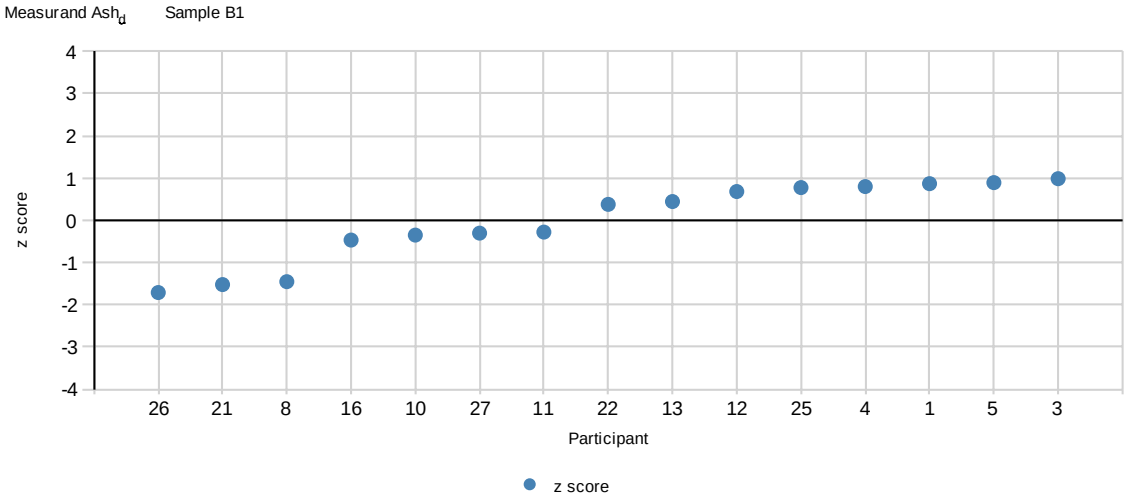
Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
Ash_d	B1	S	.	S	S	S	.	.	S	.	S	S	S	S	.	.	S	.	.	.	.	S	S	.	100
	B2	S	.	.	S	S	.	S	S	.	*u*	S	S	S	S	S	S	.	S	.	.	S	S	.	94,7
	K1	S	.	.	q	S	S	S	.	S	.	S	.	.	S	S	Q	S	.	S	S	S	S	.	89,5
C_d	B1	S	.	.	S	S	.	.	u	.	.	S	.	.	.	.	.	.	.	.	.	.	S	.	87,5
	B2	S	S	.	S	S	.	S	.	.	.	S	.	.	U	S	.	.	.	.	.	.	S	.	91,7
	K1	S	.	.	S	S	S	S	.	S	.	S	.	.	Q	S	.	.	.	S	.	.	S	.	92,9
EF	B1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	B2	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	K1	S	.	.	S	S	.	S	.	S	.	S	.	.	S	.	.	.	.	.	.	.	S	.	100
H_d	B1	S	.	.	S	q	.	.	.	.	.	S	.	.	.	.	.	.	.	.	.	.	S	.	85,7
	B2	Q	.	.	S	q	.	S	.	.	.	S	.	.	u	S	.	.	.	.	.	.	S	.	72,7
	K1	S	.	.	S	S	.	S	.	*q*	.	S	.	.	S	S	.	.	.	.	.	.	S	.	91,7
$M_{ad,d}$	B1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	B2	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	K1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
N_d	B1	S	.	.	S	S	.	.	.	.	.	S	.	.	.	.	.	.	.	.	.	.	S	.	100
	B2	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	K1	S	.	.	S	S	.	S	.	.	.	S	.	.	.	S	.	.	.	.	.	.	S	.	90,0
$q_{p,net,d}$	B1	S	.	S	S	u	.	.	.	.	S	S	S	S	.	.	*u*	.	.	.	.	.	S	.	81,8
	B2	S	.	.	S	u	.	*q*	.	.	S	S	S	S	U	S	*u*	.	S	.	.	.	S	.	75,0
	K1	S	.	.	S	u	.	S	.	S	.	S	.	.	S	S	*u*	.	.	S	.	.	S	.	84,6
$q_{V,gr,d}$	B1	S	.	S	S	S	.	.	.	.	S	S	S	S	.	.	*u*	.	.	.	.	S	S	.	92,9
	B2	S	*u*	.	S	S	.	*u*	.	.	S	S	S	S	S	S	*u*	.	S	.	.	S	S	S	85,7
	K1	S	.	.	S	S	S	q	.	S	.	S	.	.	S	S	*u*	u	.	S	S	S	S	.	84,2
S_d	B1	S	.	.	S	S	.	.	S	.	.	S	.	.	.	.	.	.	.	.	.	S	S	.	100
	K1	S	.	.	S	S	S	S	.	S	.	S	.	.	S	S	.	S	.	S	.	S	S	.	100
V_{db}	B1	S	.	.	S	Q	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	S	S	.	87,5
	B2	S	.	.	S	S	.	.	.	.	.	.	.	.	.	S	.	.	.	.	.	*u*	S	.	90,0
	K1	S	.	.	S	S	S	.	.	S	.	.	.	.	.	S	.	S	.	S	q	*u*	S	.	86,7
%		96	50	100	96	74	100	77	75	88	83	100	100	100	67	100	22	75	100	100	67	82	100	100	
accredited		23	1	3	22	22	2	7	4	5		19		6	9	8		4	3		3		20	1	

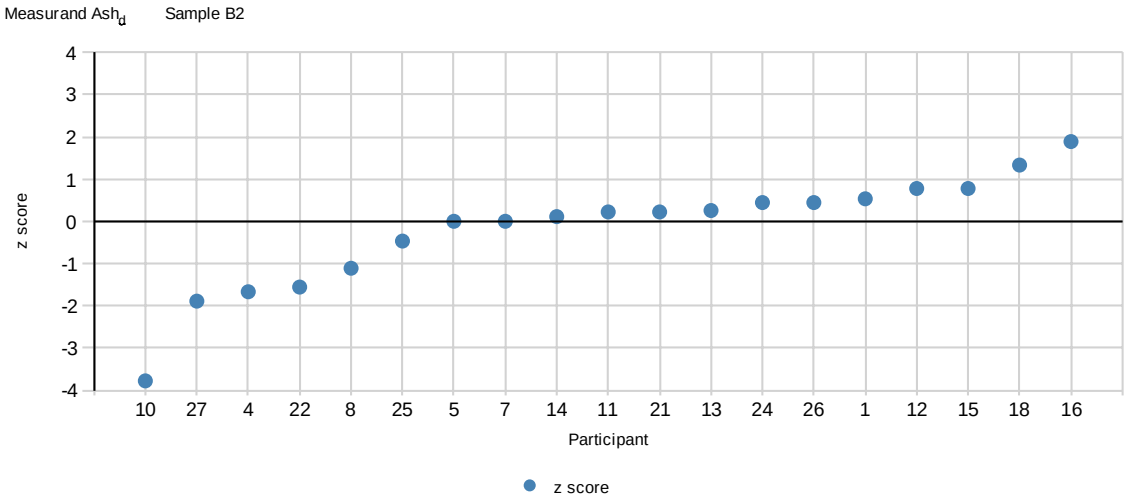
Measurand	Sample	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	%
Ash_d	B1	.	S	S	*S*	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	100
	B2	*S*	S	S	*S*	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	94,7
	K1	*S*	S	S	*S*	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	89,5
C_d	B1	.	S	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	87,5
	B2	S	S	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	91,7
	K1	*S*	S	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	92,9
EF	B1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	B2	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	K1	.	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	100
H_d	B1	.	S	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	85,7
	B2	S	S	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	72,7
	K1	*S*	S	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	91,7
$M_{ad,d}$	B1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	B2	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	K1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
N_d	B1	.	S	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	100
	B2	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	K1	*U*	S	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	90,0
$q_{p,net,d}$	B1	.	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	81,8
	B2	S	S	.	.	*S*	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	75,0
	K1	*S*	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	84,6
$q_{V,gr,d}$	B1	.	S	S	*S*	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	92,9
	B2	S	S	S	*S*	*S*	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	85,7
	K1	*S*	S	S	*S*	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	84,2
S_d	B1	.	S	*S*	*S*	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	100
	K1	*S*	S	S	*S*	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	100
V_{db}	B1	.	S	S	*S*	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	87,5
	B2	*S*	S	S	*S*	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	90,0
	K1	*S*	S	S	*S*	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	86,7
%		93	100	100	100	100																			
accredited		4	23	18																					

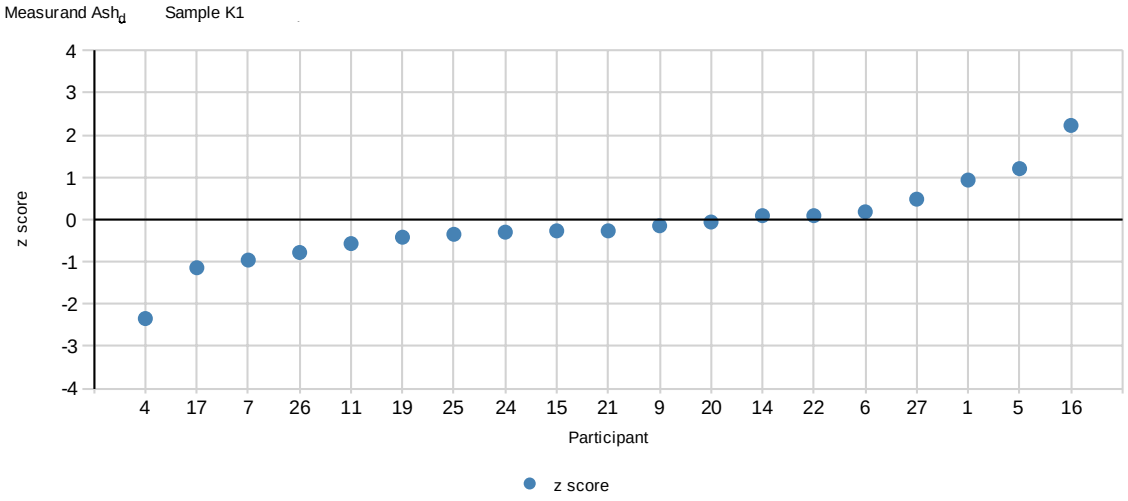
S - satisfactory ($-2 \leq z \leq 2$), Q - questionable ($2 < z < 3$), q - questionable ($-3 < z < -2$),
U - unsatisfactory ($z \geq 3$), and u - unsatisfactory ($z \leq -3$), respectively
bold - accredited, italics - non-accredited, normal - other
% - percentage of satisfactory results

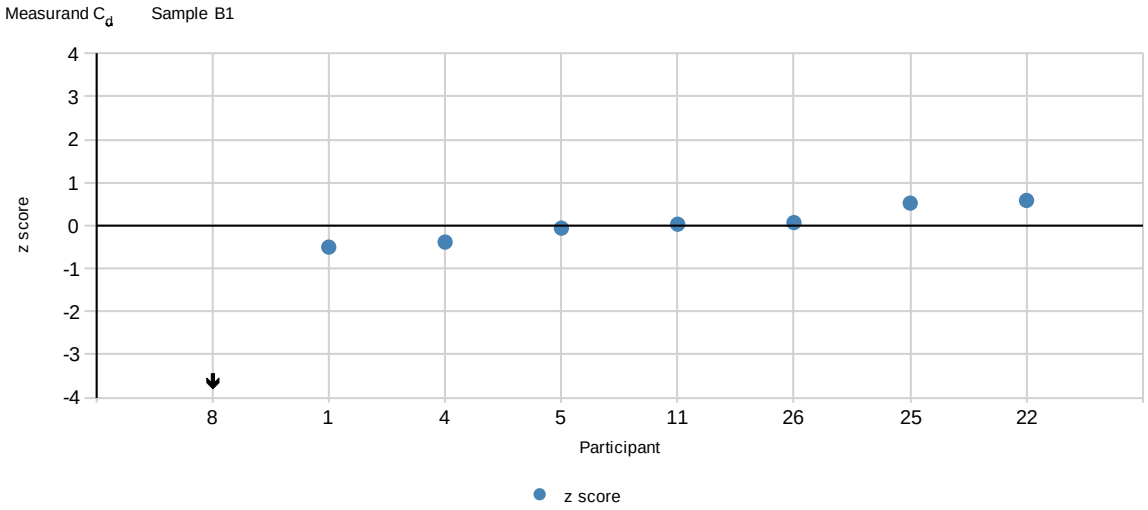
Totally satisfactory, % in all: 90 % in accredited: 92 % in non-accredited: 83

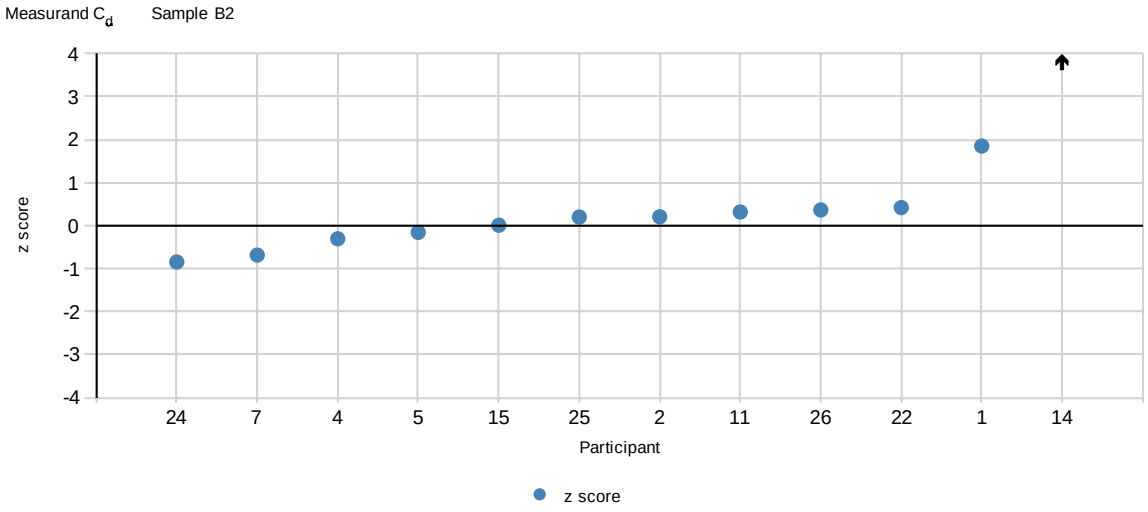
APPENDIX 9: z scores in ascending order

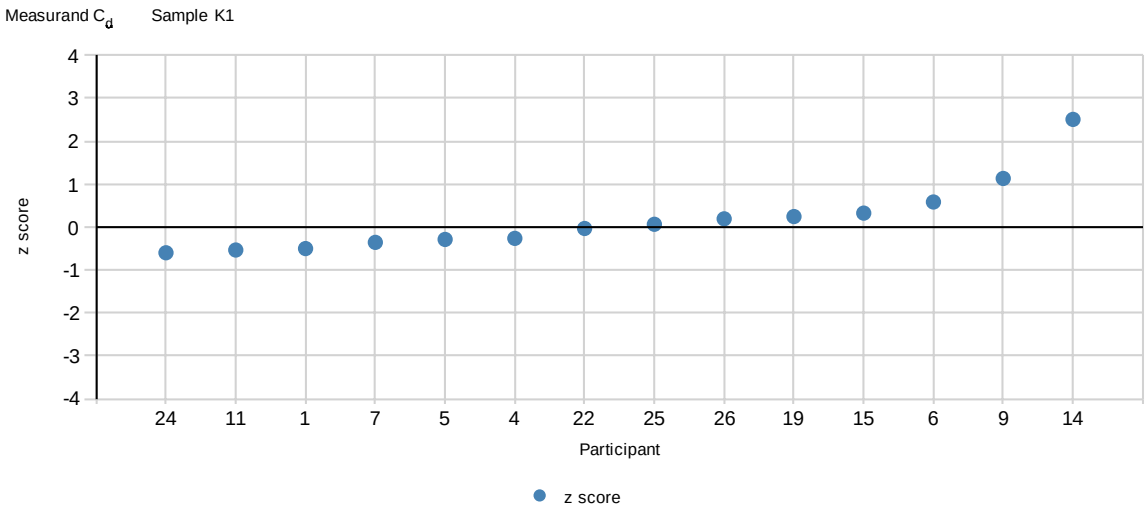




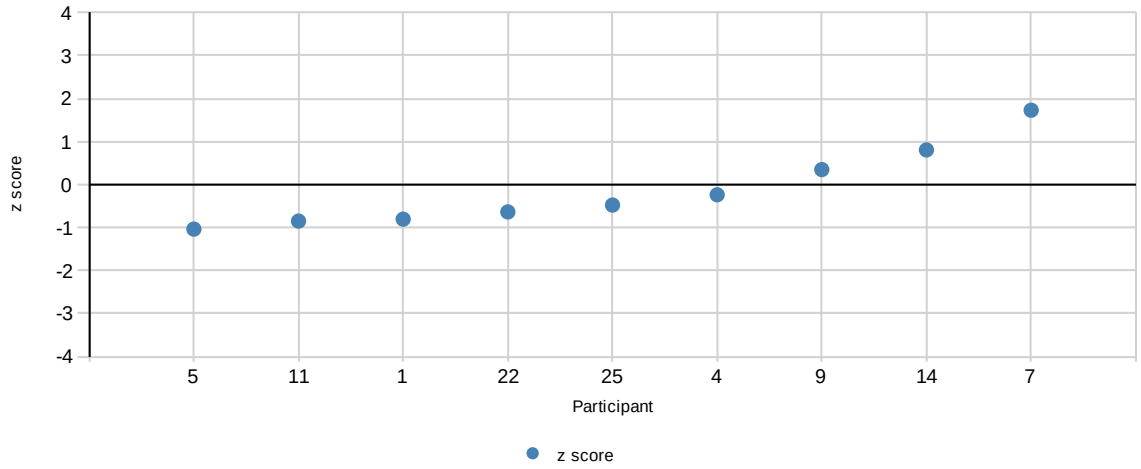



Measurand C_d Sample B1
z score
4
3
2
1
0
-1
-2
-3
-4
8
1
4
5
11
26
25
22
Participant
z score

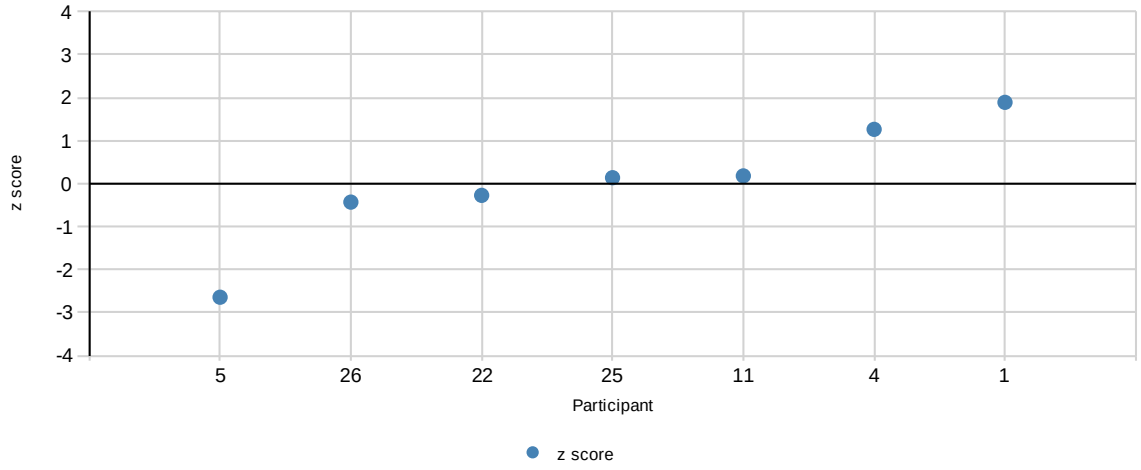

Measurand C_d Sample B2
z score
4
3
2
1
0
-1
-2
-3
-4
24
7
4
5
15
25
2
11
26
22
1
14
Participant
z score


Measurand C_d Sample K1
z score
4
3
2
1
0
-1
-2
-3
-4
24
11
1
7
5
4
22
25
26
19
15
6
9
14
Participant
z score

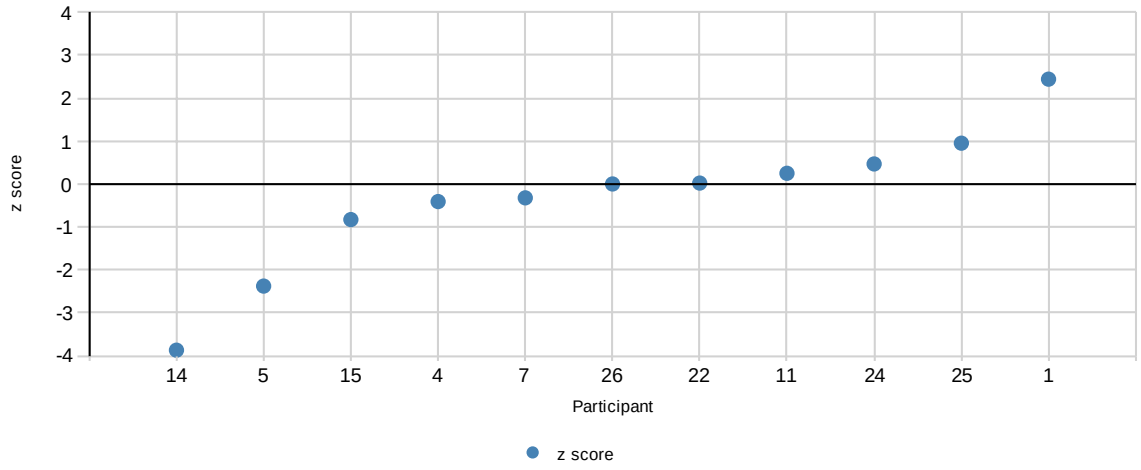
Measurand EF Sample K1

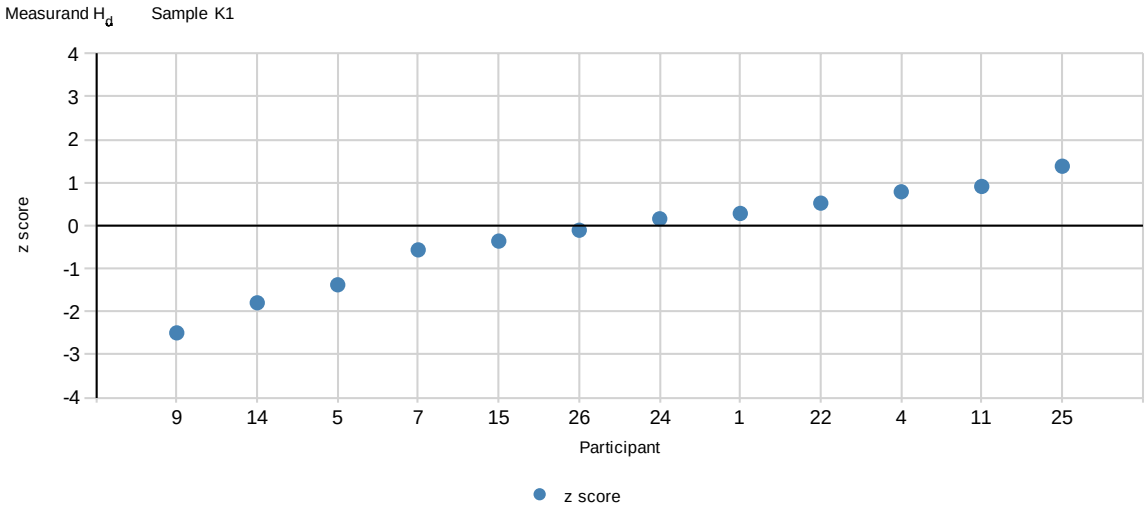


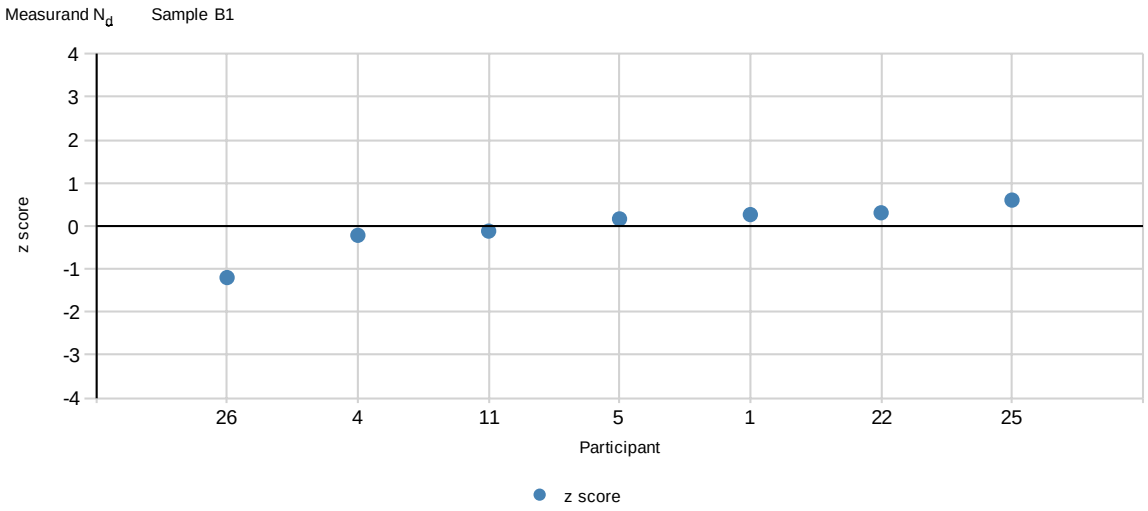
Measurand H_d Sample B1

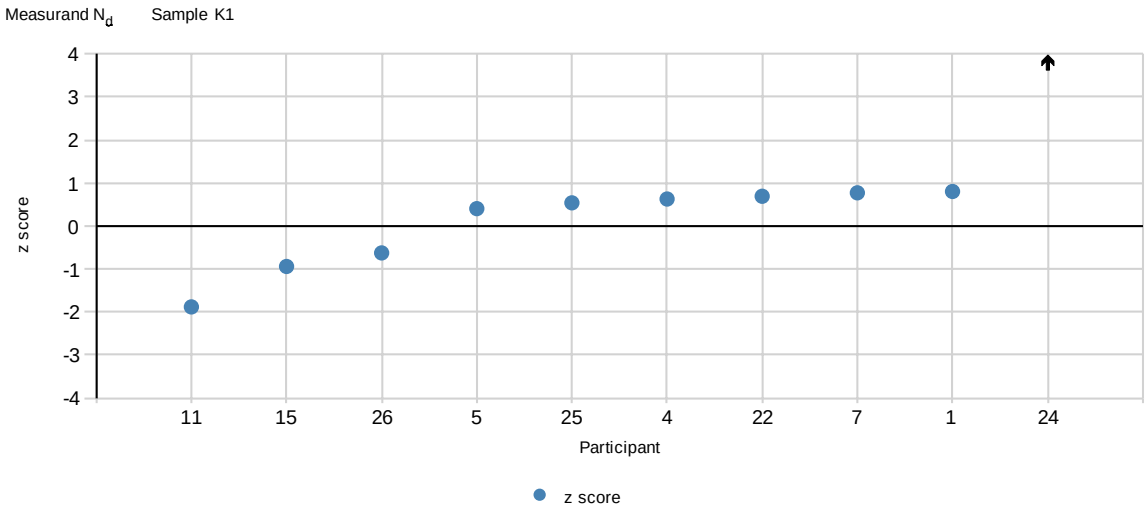


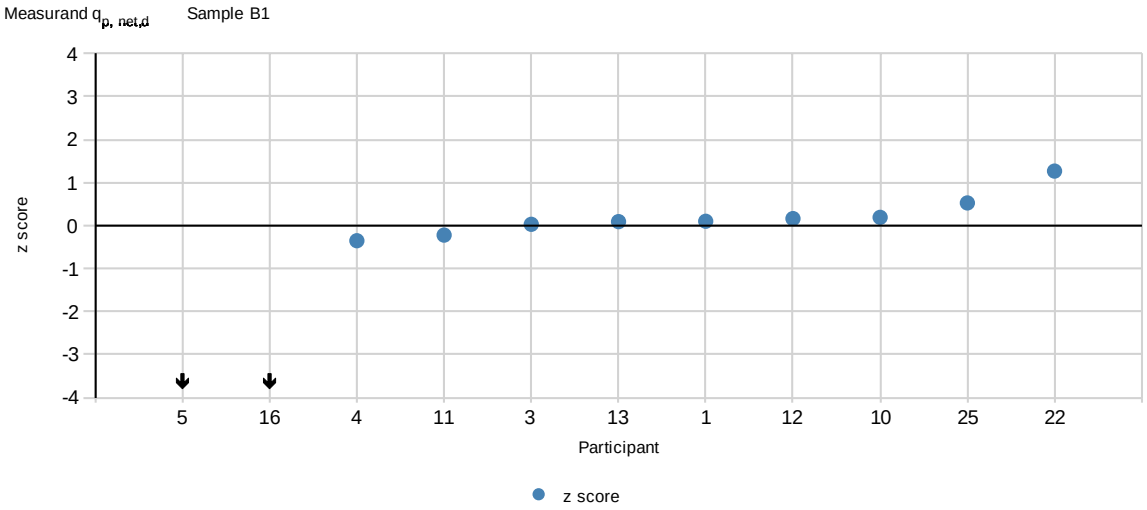
Measurand H_d Sample B2

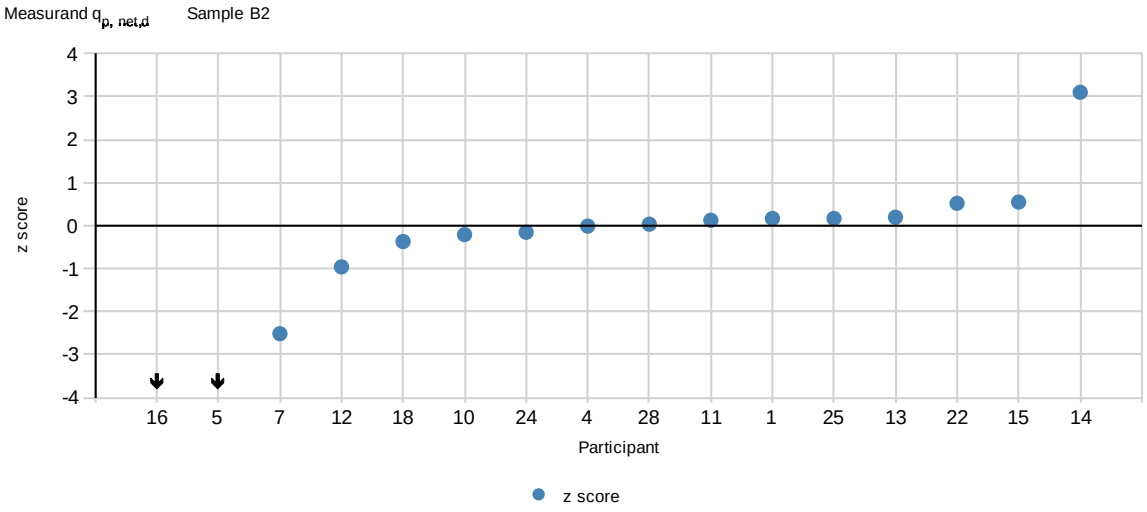


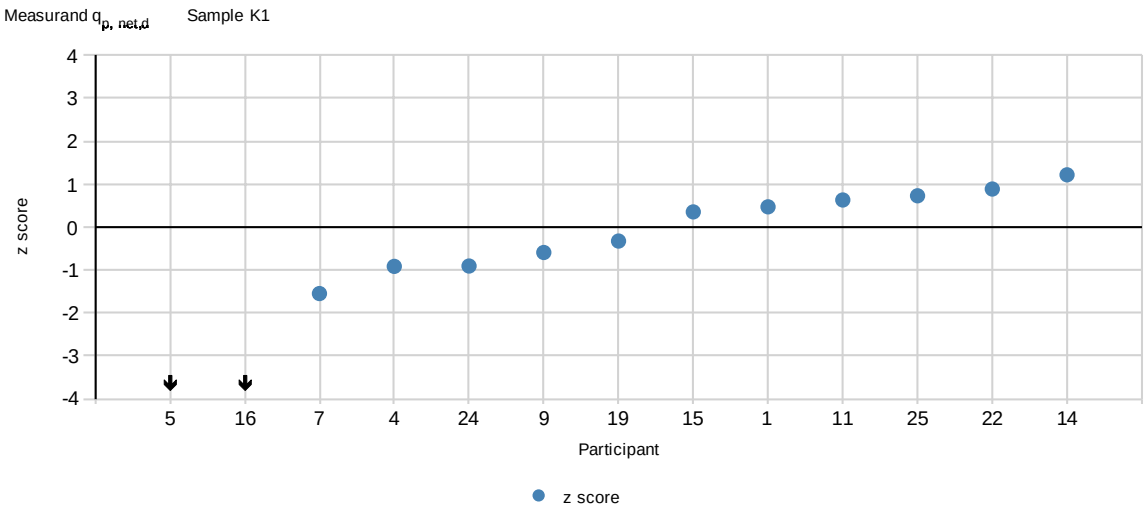

Measurand H_d Sample K1
z score
4
3
2
1
0
-1
-2
-3
-4
9
14
5
7
15
26
24
1
22
4
11
25
Participant
z score

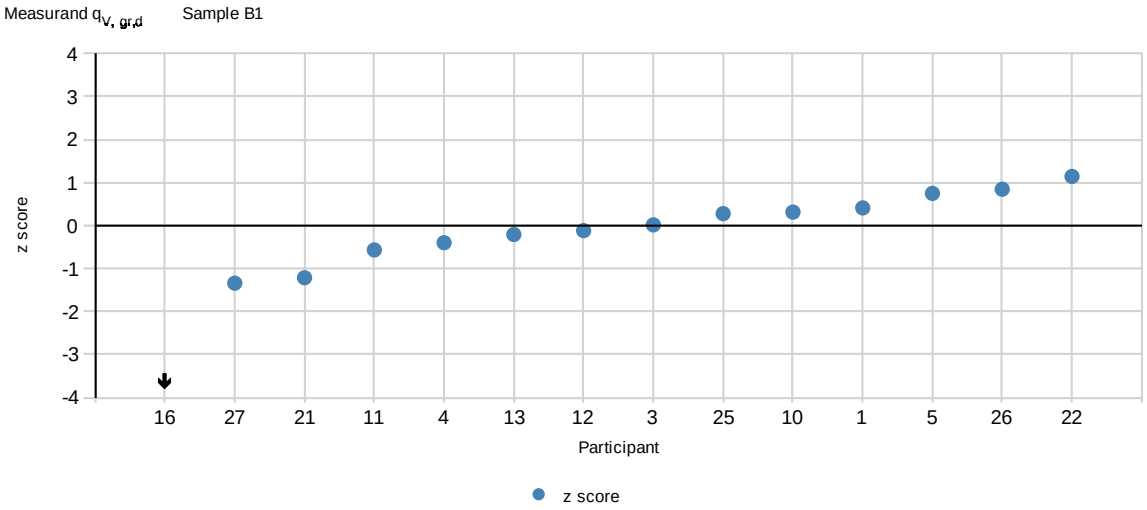

Measurand N_d Sample B1
z score
4
3
2
1
0
-1
-2
-3
-4
26
4
11
5
1
22
25
Participant
z score

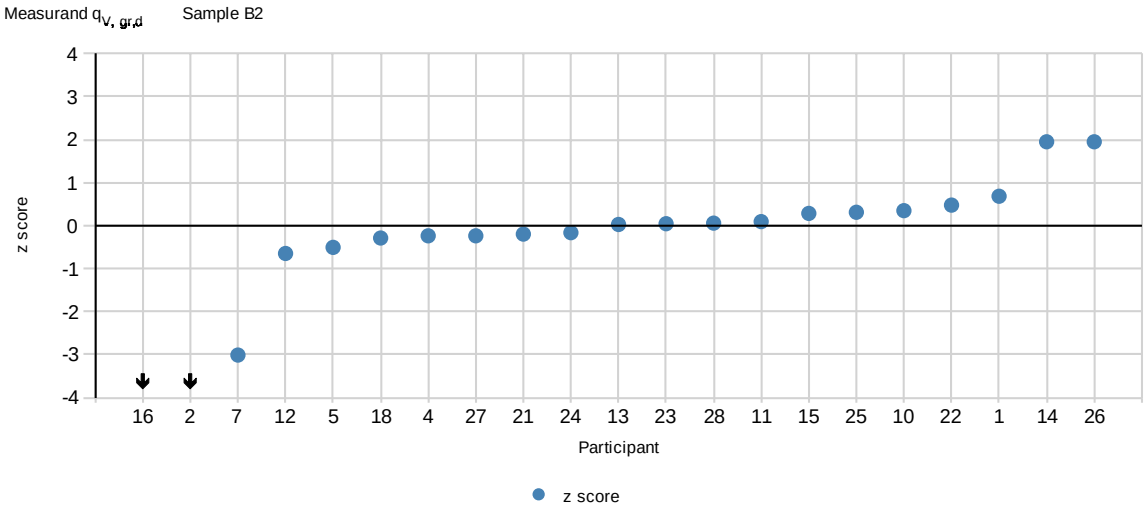

Measurand N_d Sample K1
z score
4
3
2
1
0
-1
-2
-3
-4
11
15
26
5
25
4
22
7
1
24
Participant
z score

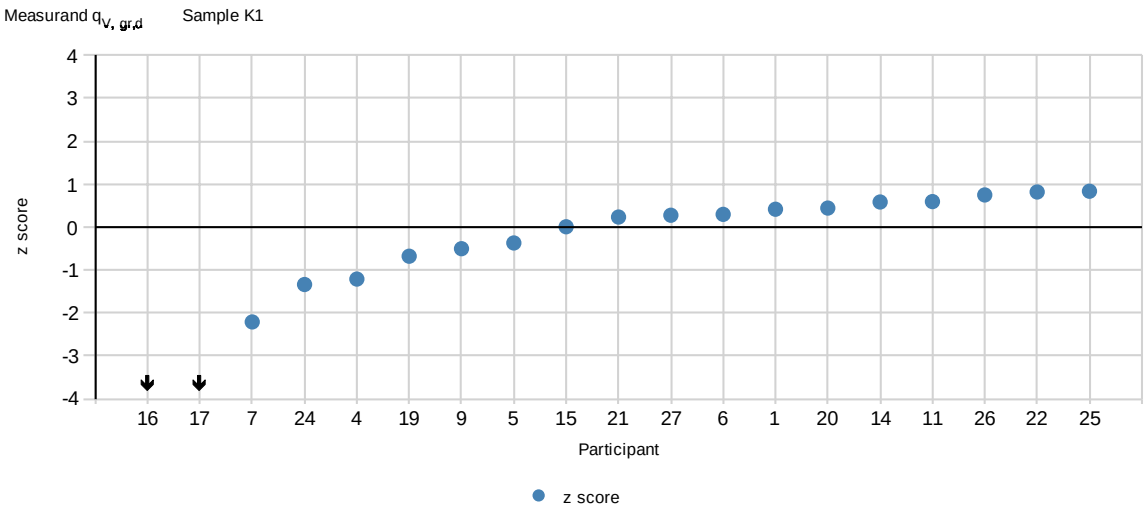

Measurand $q_{p,\ net,d}$
Sample B1
z score
4
3
2
1
0
-1
-2
-3
-4
5
16
4
11
3
13
1
12
10
25
22
Participant
z score

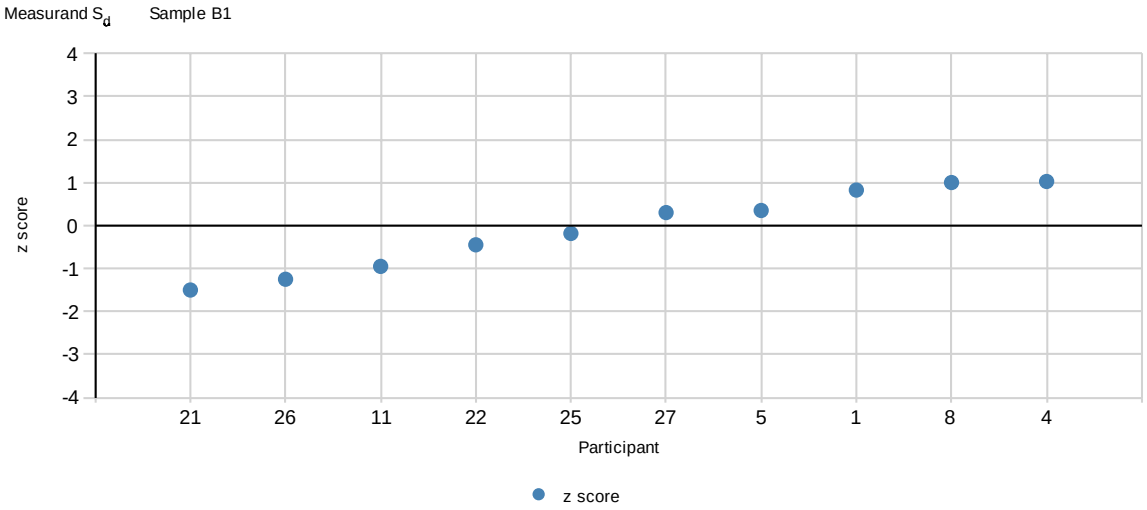

Measurand $q_{p,\ net,d}$
Sample B2
z score
4
3
2
1
0
-1
-2
-3
-4
16
5
7
12
18
10
24
4
28
11
1
25
13
22
15
14
Participant
z score

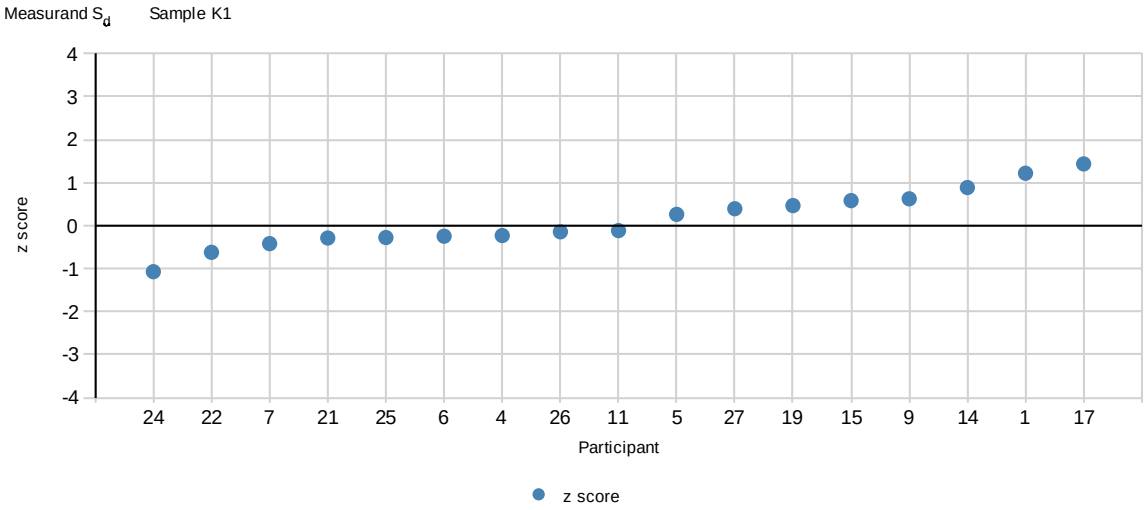

Measurand $q_{p,\ net,d}$
Sample K1
z score
4
3
2
1
0
-1
-2
-3
-4
5
16
7
4
24
9
19
15
1
11
25
22
14
Participant
z score

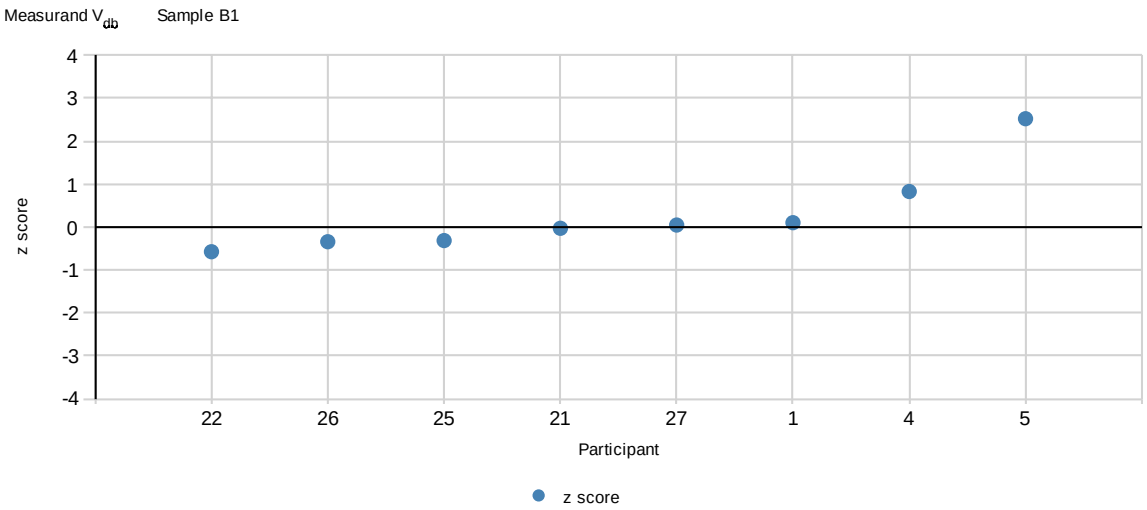

Measurand $q_{V,\,gr,d}$
Sample B1
z score
4
3
2
1
0
-1
-2
-3
-4
16 27 21 11 4 13 12 3 25 10 1 5 26 22
Participant
z score

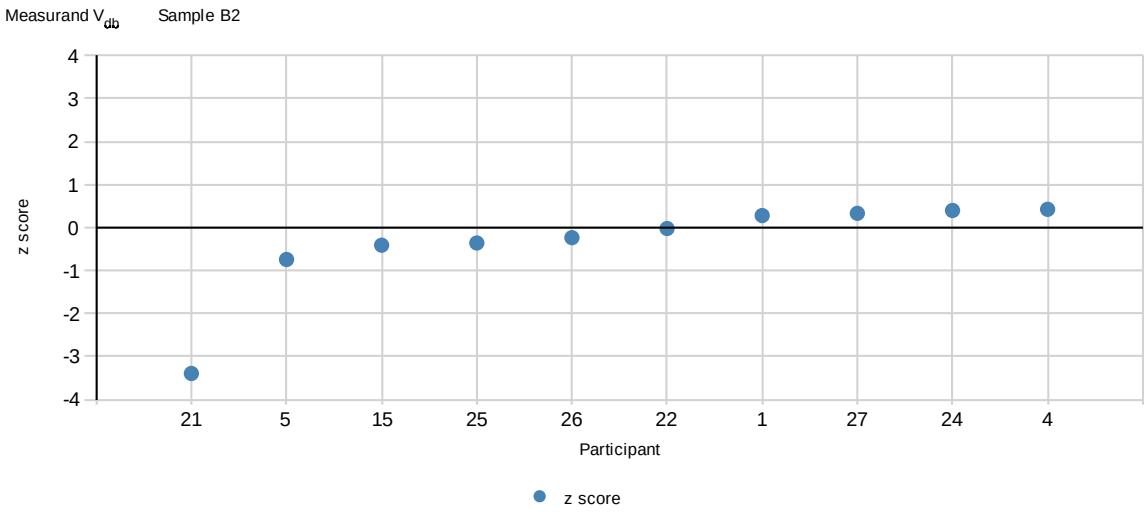

Measurand $q_{V,\,gr,d}$
Sample B2
z score
4
3
2
1
0
-1
-2
-3
-4
16 2 7 12 5 18 4 27 21 24 13 23 28 11 15 25 10 22 1 14 26
Participant
z score

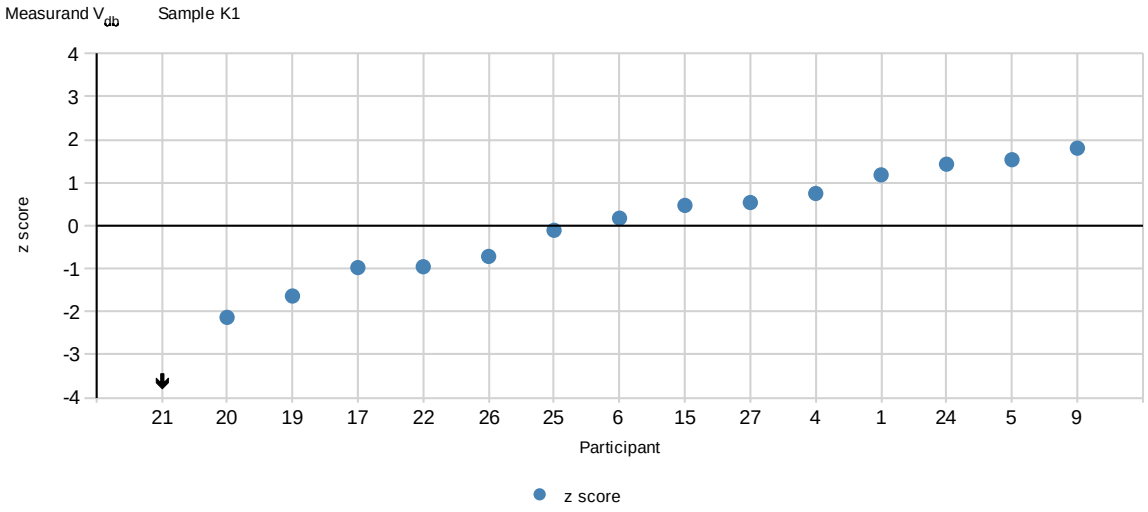

Measurand $q_{V,\,gr,d}$
Sample K1
z score
4
3
2
1
0
-1
-2
-3
-4
16 17 7 24 4 19 9 5 15 21 27 6 1 20 14 11 26 22 25
Participant
z score


Measurand S_d Sample B1
z score
4
3
2
1
0
-1
-2
-3
-4
21
26
11
22
25
27
5
1
8
4
Participant
z score


Measurand S_d Sample K1
z score
4
3
2
1
0
-1
-2
-3
-4
24
22
7
21
25
6
4
26
11
5
27
19
15
9
14
1
17
Participant
z score


Measurand V_{db} Sample B1
z score
4
3
2
1
0
-1
-2
-3
-4
22
26
25
21
27
1
4
5
Participant
z score


Measurand V_{db}
Sample B2
z score
4
3
2
1
0
-1
-2
-3
-4
21
5
15
25
26
22
1
27
24
4
Participant
z score


Measurand V_{db}
Sample K1
z score
4
3
2
1
0
-1
-2
-3
-4
21
20
19
17
22
26
25
6
15
27
4
1
24
5
9
Participant
z score

APPENDIX 10: Analytical measurements and background information for calculations

Reported details of the measurements:

Measurement of gross calorific value	Sample B1 (peat)	Sample B2 (wood pellet)	Sample K1 (coal)
Sample amount:	0.9 – 2.5 g	0.8 – 2.5 g	0.9 – 2.5 g
Air dried samples:	participants 1, 22, 27	participants 1, 7, 22, 24, 27, 28	participants 1, 6, 7, 9, 22, 24, 25, 27, 28
Drying in 105 °C:	participants 4, 25	participants 4, 8, 18, 25	participants 4, 19, 20
Other:	participant 8: 108°C	-	-
Equipment:	PARR (models 6200, 6300, 6400): participants 6, 7, 18, 22, 24, 28		
	LECO (model AC350, AC600): participants 1, 25, 17, 27		
	IKA (models C2000, C5000): participants 1, 4, 9, 19, 20		
Other:	participant 8: out of service		

Correction taken into account in calculations:

Gross calorific value			
Participants and correction factors used	Sample		
	B1 (peat)	B2 (wood pellet)	K1 (coal)
1: wire, ignition, acid correction, analysis moisture	x	x	x
1: S	x		x
4: wire, ignition, S, analysis moisture	x	x	x
6: wire, ignition, S, acid correction, analysis moisture			x
7: wire, N, analysis moisture		x	x
7: S			x
9: wire, ignition, S, analysis moisture			x
18: wire, ignition, S, acid correction, analysis moisture		x	
19: wire, acid correction			x
20: wire, ignition			x
24: wire, S, acid correction, analysis moisture		x	x
25: wire, S, acid correction	x	x	x
25: analysis moisture			x
27: wire, S, N, analysis moisture	x	x	x
28: analysis moisture		x	

Correction taken into account in calculations:

Net calorific value (literature value in brackets)			
Participant	Sample		
	B1 (peat)	B2 (wood pellet)	K1 (coal)
1	N+O, H	N+O, H	N+O, H
4	N+O, H	N+O	N+H
6			H
7		N+O, H	N+O , H
9			H
18		N+O (43+0,1%), H (6,2)	
19			N+O, H calculated, N+O (ISO 17247), H (ISO 1928)
22		N+O, H	N+O, H
24		N+O, H	N+O, H
25	N+O, H	N+O, H	N+O, H
28		H	

Methods used in ash and moisture measurements:

Measurement	Method	°C	Sample B1 (peat)	Sample B2 (wood pellet)	Sample K1 (coal)
Ash content (ashing temperature ℃)	Gravimetric	550	parts 1, 4, 22, 25, 27	parts 1, 4, 7, 22, 24, 25, 27	
		815			parts 1, 4, 7, 9, 17, 20, 22, 24, 25, 27
	TGA:	250+550		part 8	
		550		parts 18, 28	
		750			part 6
		815	part 8		part 19
Moisture content of analysis sample, M_{ad} (temperature °C)	Air:		parts 1, 4, 22, 25, 27	parts 1, 4, 7, 18, 22, 24, 25, 27	parts 4, 7, 17, 20, 24, 27
	N_2 atmosphere:			part 28	parts 1, 6, 9, 19, 22, 25
	Gravimetric:	103		part 24	
		105	parts 1, 4, 22, 25, 27	parts 1, 4, 7, 22, 25, 27	parts 1, 4, 7, 20, 27
		107			parts 9, 17, 24, 25
		107.5			part 22
	TGA:	105		parts 18, 19	part 6
		107		part 28	
Relative humidity of analyzing room (%)	part 1: 41,5, part 4: 20-30, part 6: 26, part 7: 40, part 9: 50, part 17: 51,6, part 18: 48, part 19: 60, part 20: 55, part 22: 27, part 24: 50, part 25: 49,6, part 27: 42, part 28: 45				

CHN-measurements carried out by:

Sample			
	B1	B2	K1
Air dried samples:	parts 4, 22, 25	parts 4, 7, 22, 24, 25, 28	parts 1, 4, 6, 7, 9, 22, 24, 25
Drying in 105 °C:	part 1	part 1	
Other:			

Detection limits in nitrogen and sulphur measurements:

Participant	Detection limit for N (w%)	Participant	Detection limit for S (w%)
1	0.1	1	0.03
4	0-100	4	0-100
7	0.050	6	0.03
22	0.03	7	0.100
24	0.01	9	0.01
25	0.05	17	0.001
28	0.01-50	19	0.10-11.5
		22	0.002
		24	0.01
		25	0.01

Calculations of Emission factor (EF)[1]:

We have used the equation based on the decision 2007/589/EC (18.7.2007).
If no, describe how?

	Sample B1 (peat)	Sample B2 (wood pellet)	Sample K1 (coal)
Yes:	parts 1, 4, 22, 25	parts 22, 28	parts 1, 4, 7, 9, 19, 22, 25
No:	part 4: the older version from 2007		part 4: the older version from 2007 part 6: part don´t use this index in practice

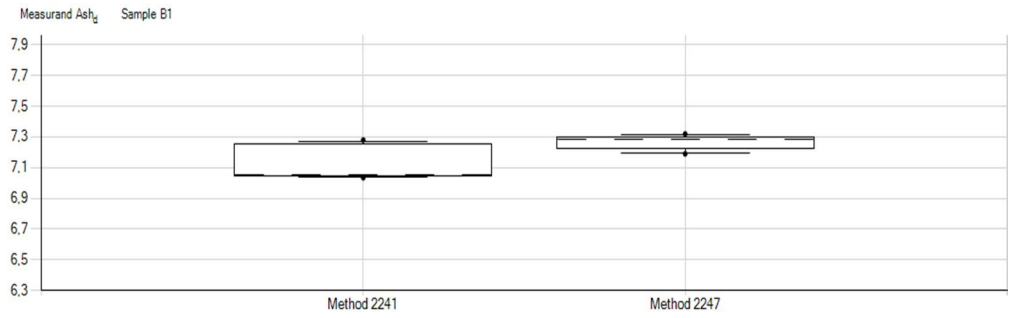
[1]In the cover letter the provider gave the participants the possibility to calculate the EF-value using the procedure presented in the EC directive and using the total moisture content as presented in the letter. Later it was obtained, that the EC directive is not giving the detailed equation for calculation of EF-values. Therefore, some national guides for the equation of EF value calculation have been produced.
As a result from this, the Energy Market Authority in Finland has made the guideline for the calculation of emission factor for fossile fuels as follows:

$EF = 1000 \times 3.664 \times (C/100) \times (1 - M_{ar}/100)/Q_{net.ar}$, where

EF emission factor, g CO_2/MJ
C carbon content as dry, %
M_{ar} total moisture as received, %
$Q_{net.ar}$ net calorific value as received, MJ/kg
(http://www.energiavirasto.fi/documents/10179/132665/Paastokertoimen+laskentaohje.pdf)

APPENDIX 11: Significant differences in the results reported using different methods

Boxplot figures: In the box the upper and lower limit included 50 % of the results. The dashed vertical line in the middle of the box is the median of the results. The vertical lines above and under the box describe the limits of 80 % of the results. The black dots describe the highest and smallest results within the center 90 % of the results.

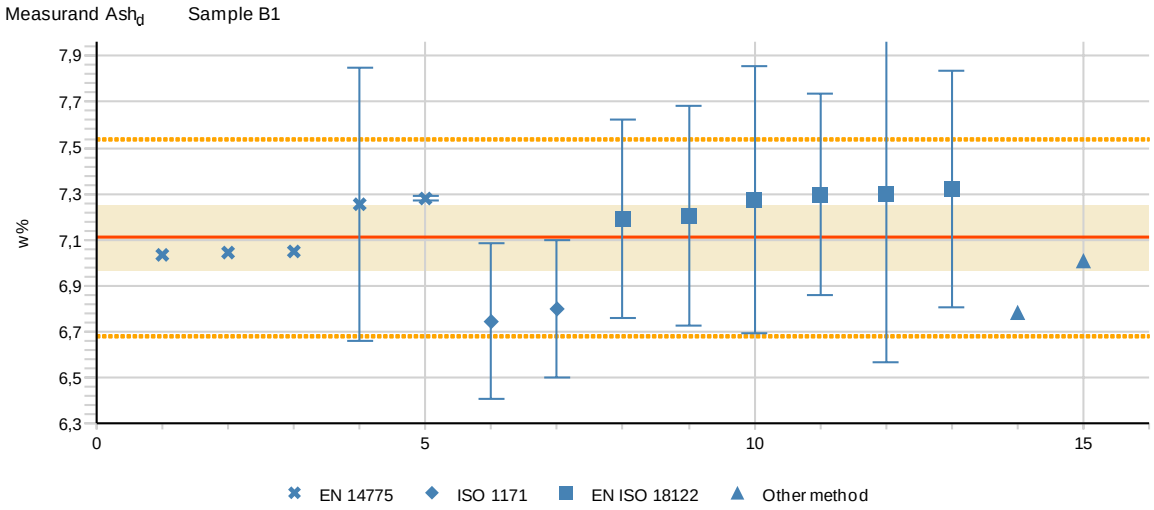


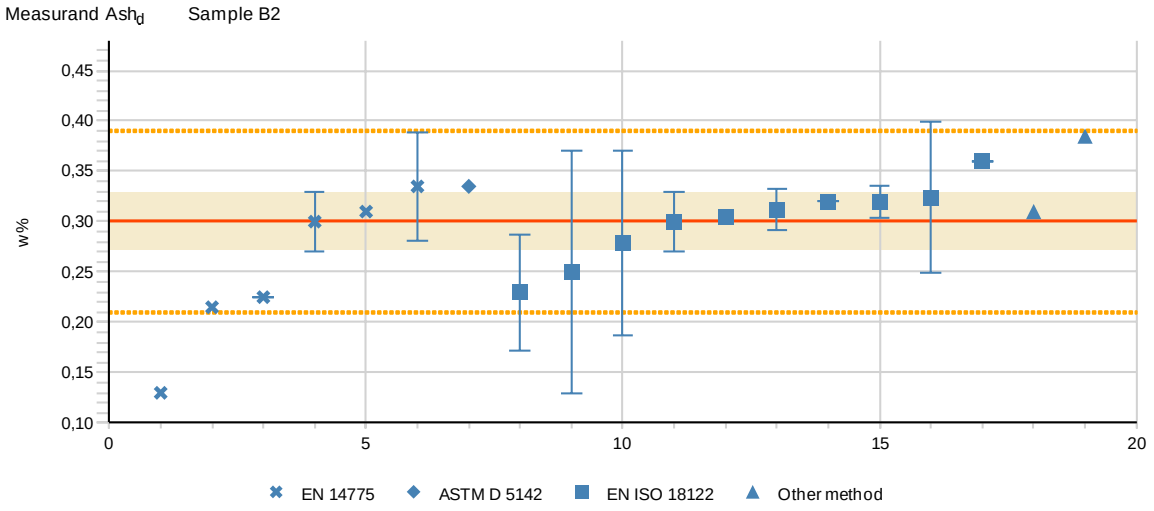
Method	n	Mean (w%)	SD (w%)
Method 2241- EN 14775	5	7.13	0,12
Method 2247 – EN ISO 18122	6	7.26	0,05

n= number of results, SD= standard deviation

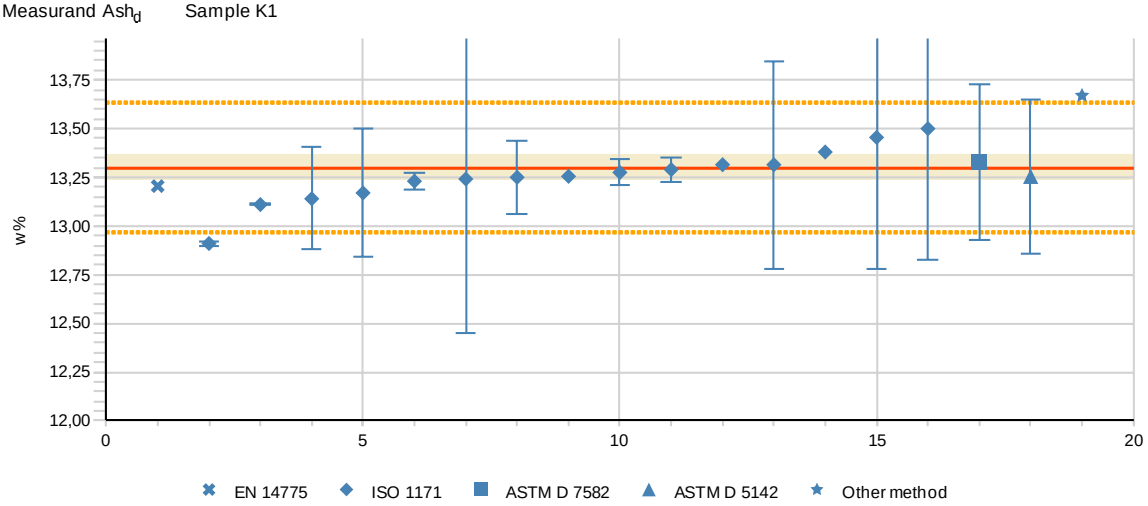
APPENDIX 12: Results grouped according to the methods

The explanations for the figures are described in the Appendix 9. The results are shown in ascending order.

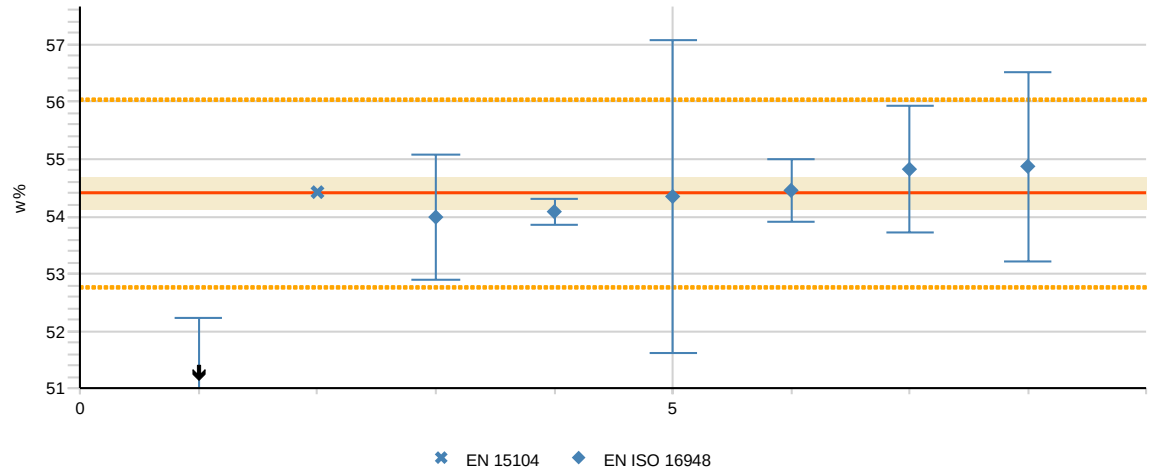




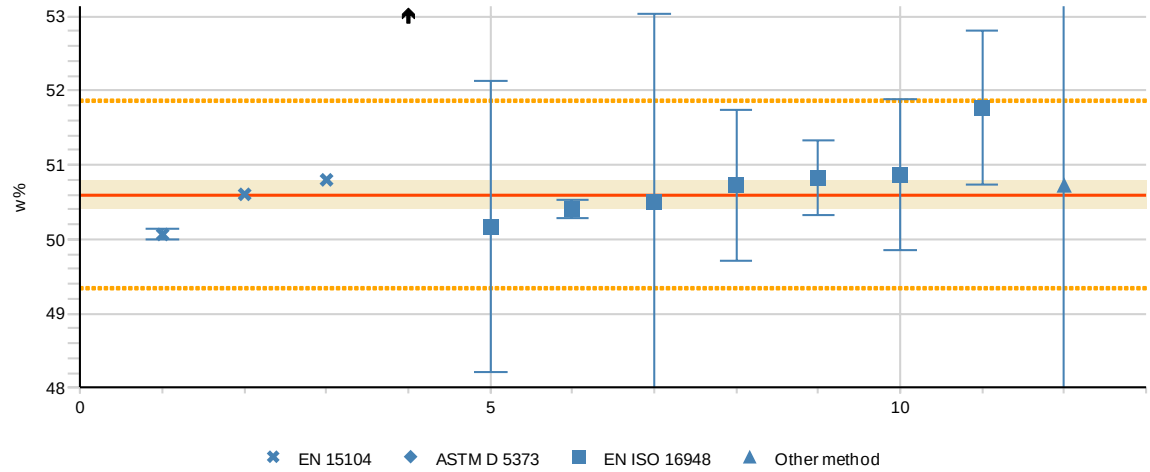
Measurand Ash_d Sample K1



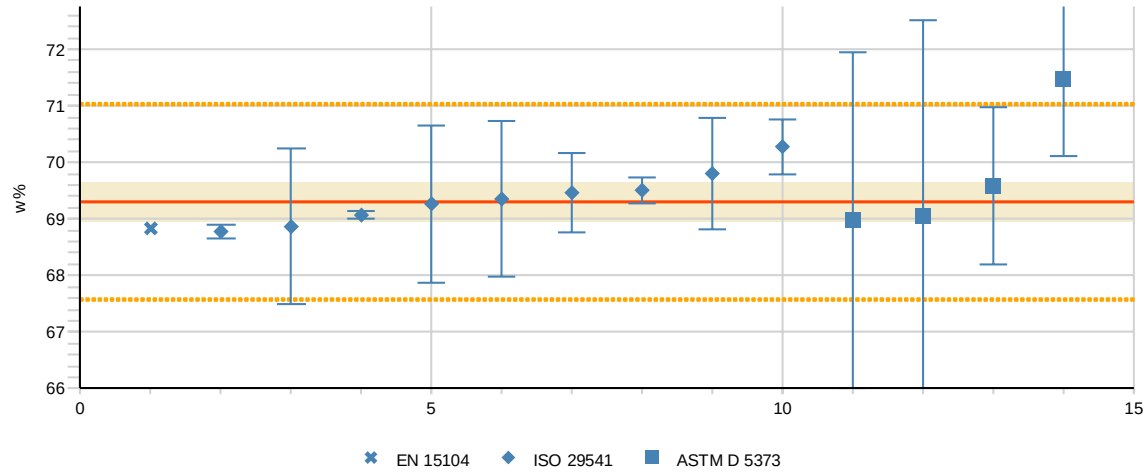
Measurand C_d Sample B1



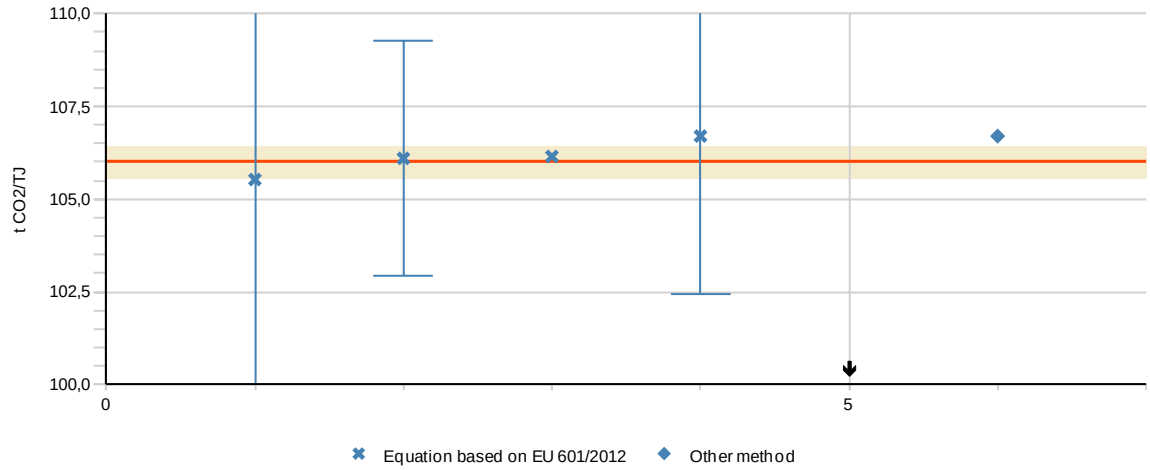
Measurand C_d Sample B2



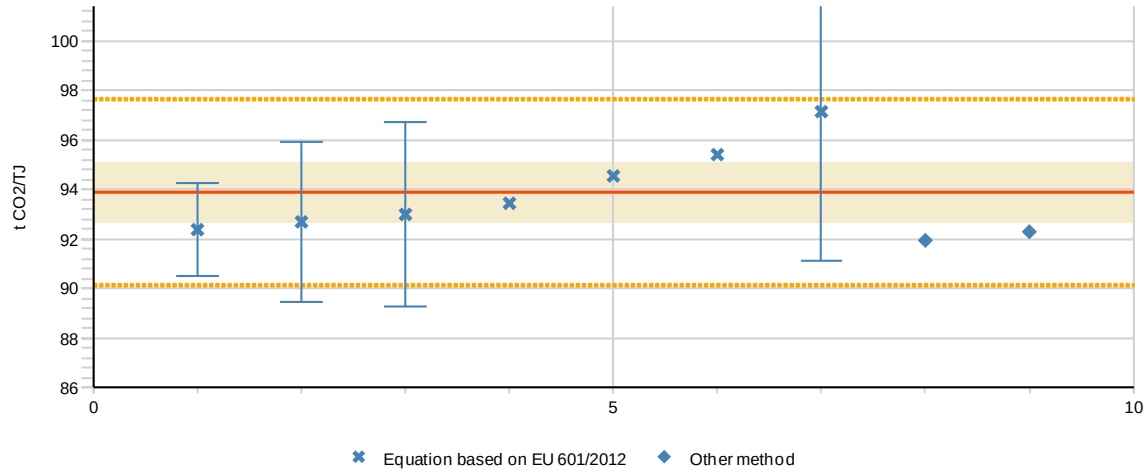
Measurand C_d Sample K1

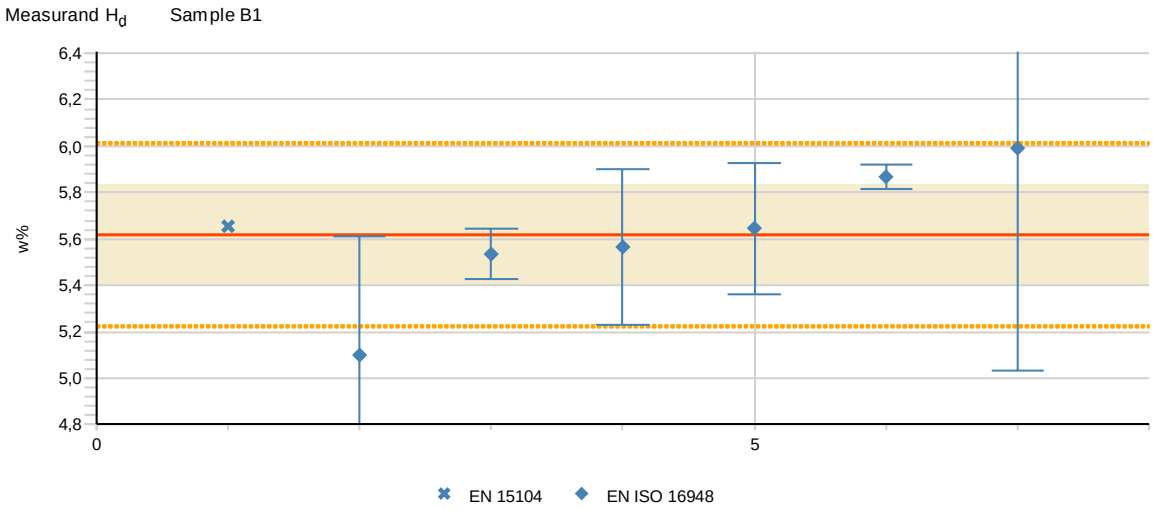


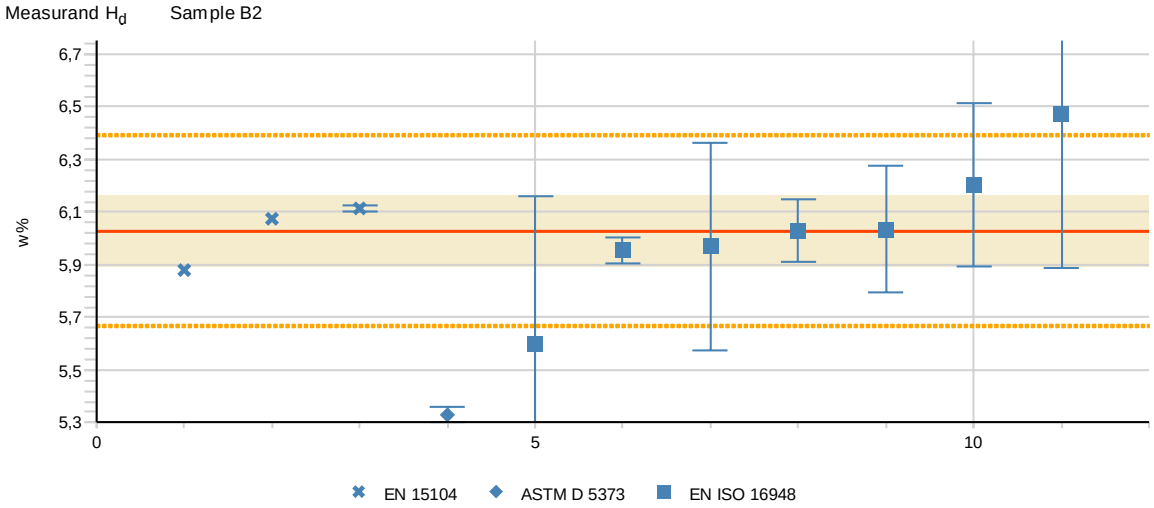
Measurand EF Sample B1

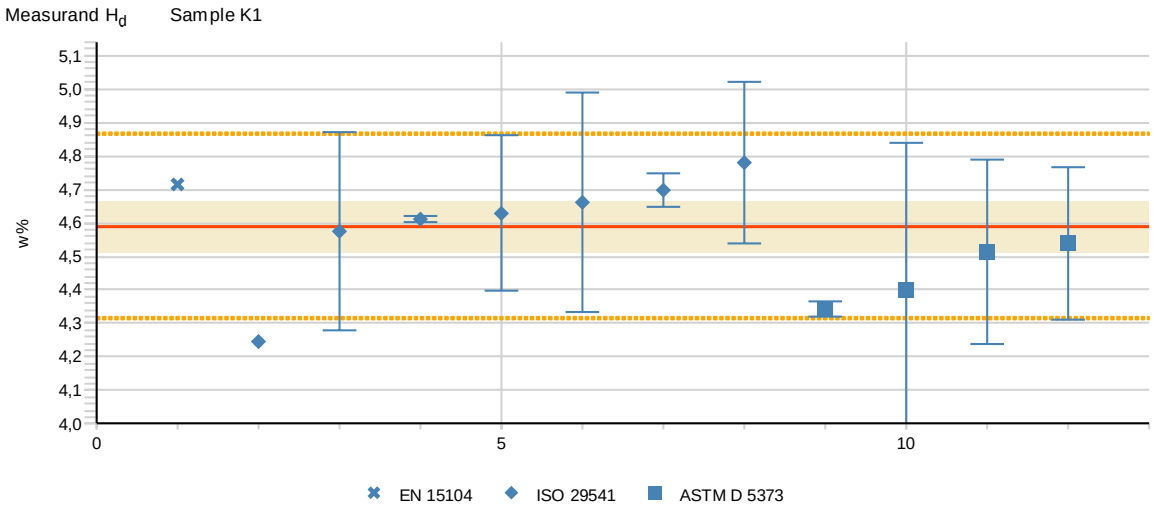


Measurand EF Sample K1

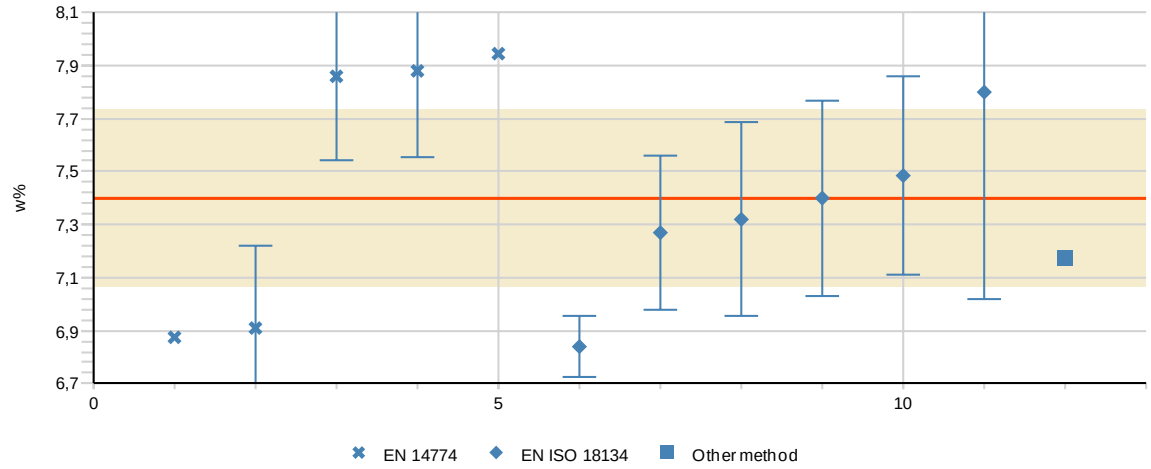



Measurand H_d
Sample B1
w%
6,4
6,2
6,0
5,8
5,6
5,4
5,2
5,0
4,8
0
5
EN 15104
EN ISO 16948

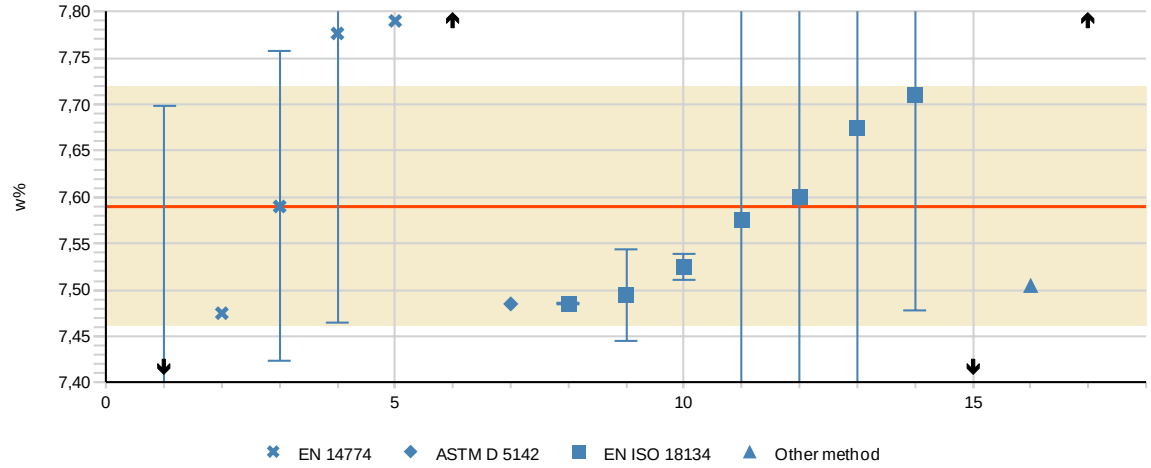

Measurand H_d
Sample B2
w%
6,7
6,5
6,3
6,1
5,9
5,7
5,5
5,3
0
5
10
EN 15104
ASTM D 5373
EN ISO 16948


Measurand H_d
Sample K1
w%
5,1
5,0
4,9
4,8
4,7
4,6
4,5
4,4
4,3
4,2
4,1
4,0
0
5
10
EN 15104
ISO 29541
ASTM D 5373

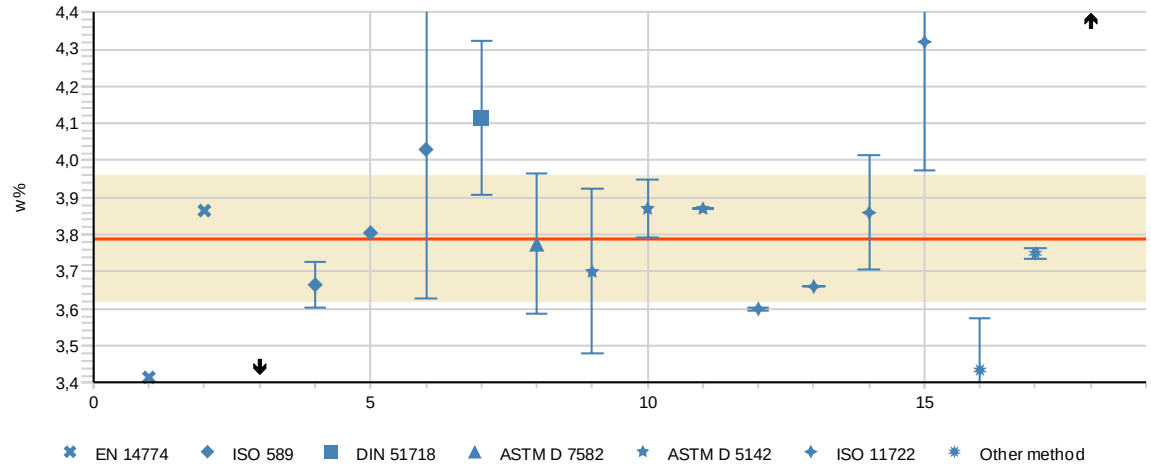
Measurand $M_{ad,d}$ Sample B1

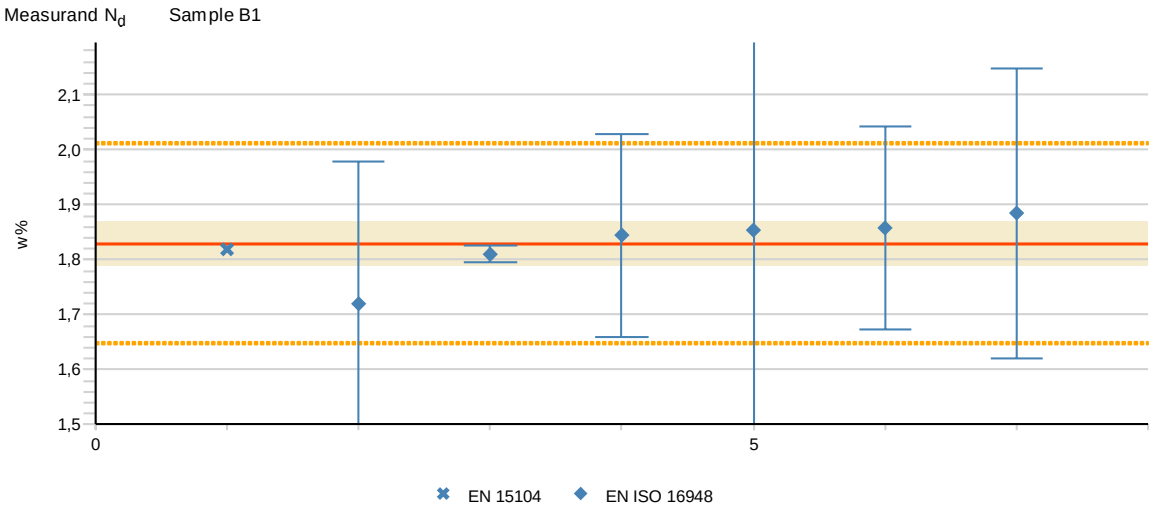


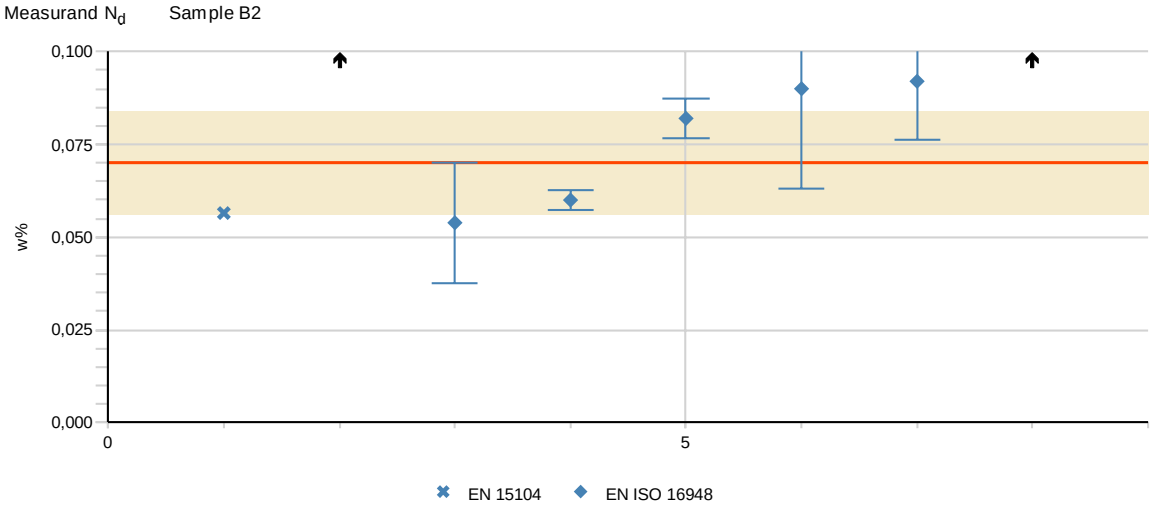
Measurand $M_{ad,d}$ Sample B2

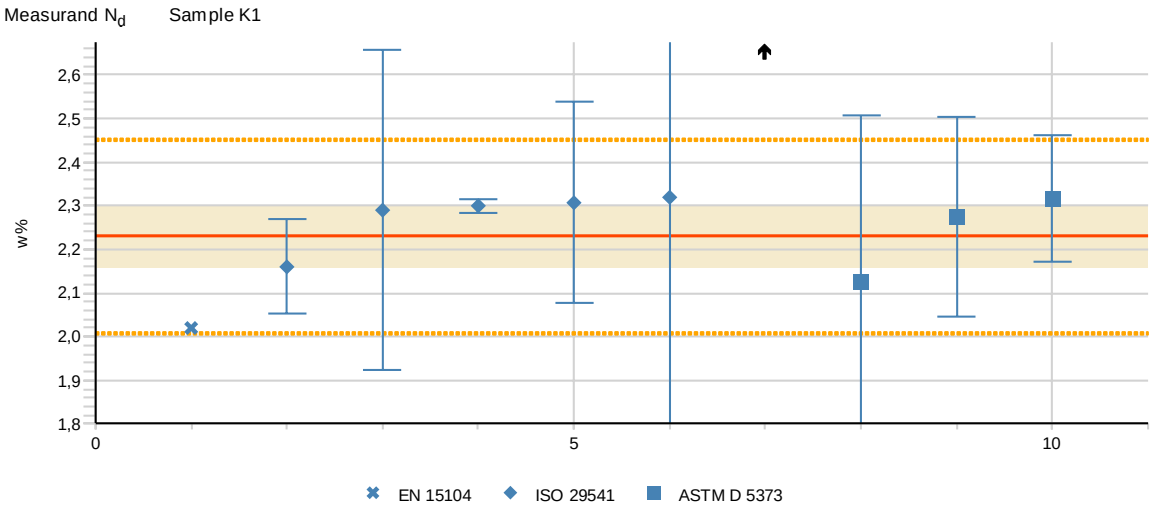


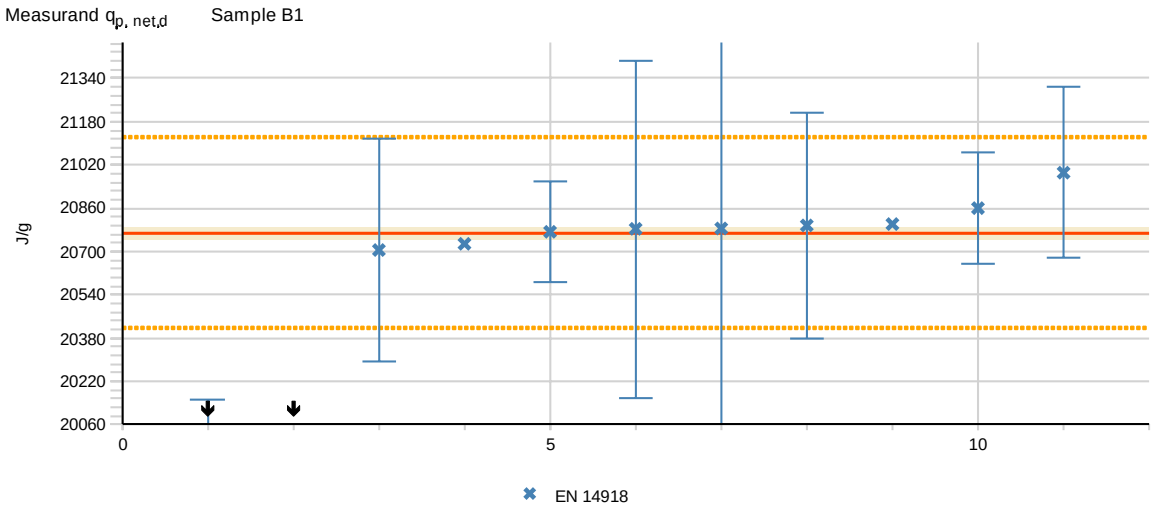
Measurand $M_{ad,d}$ Sample K1

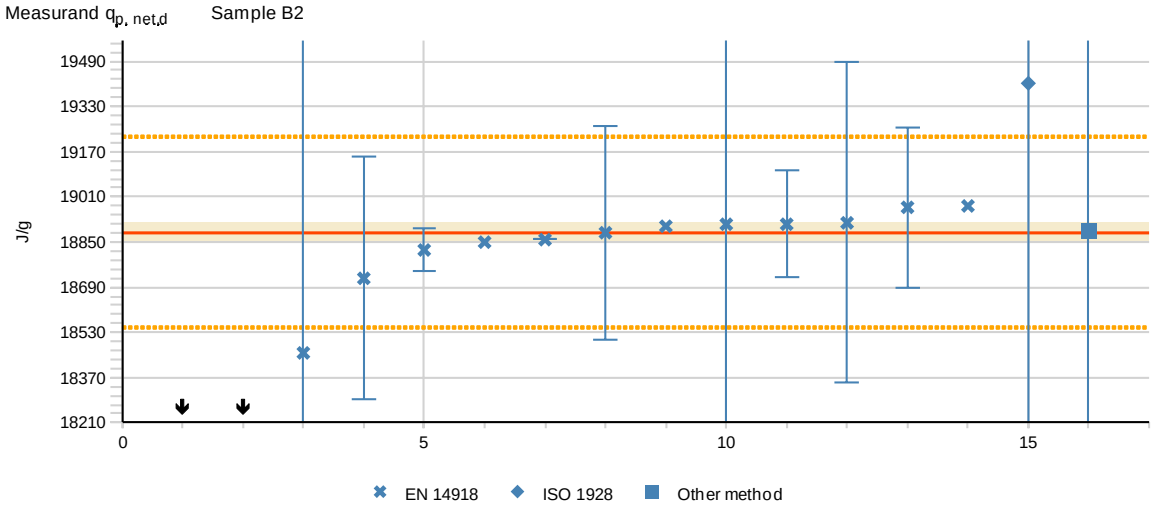


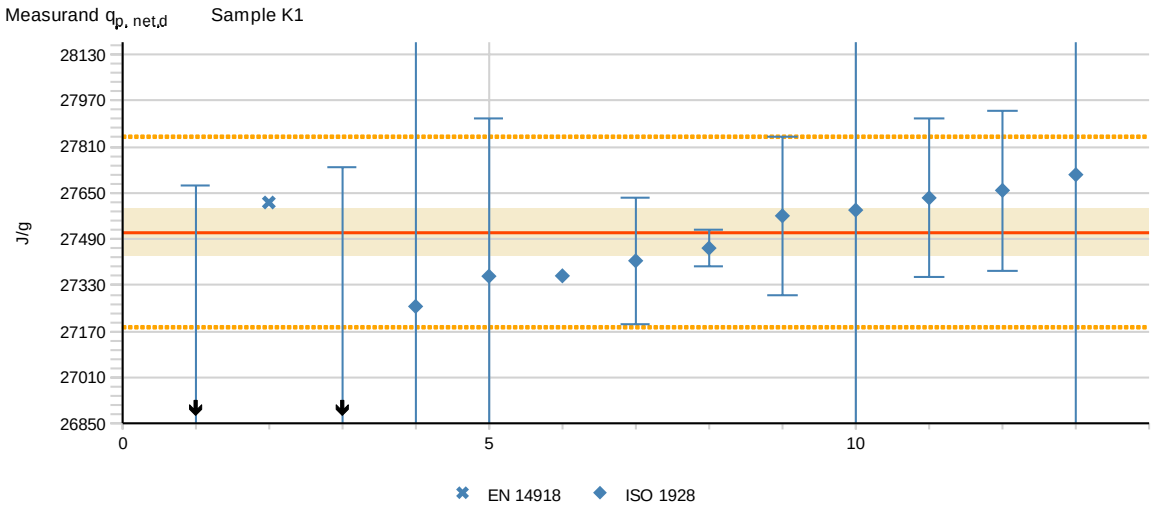

Measurand N_d
Sample B1
w%
2,1
2,0
1,9
1,8
1,7
1,6
1,5
0
5
EN 15104
EN ISO 16948

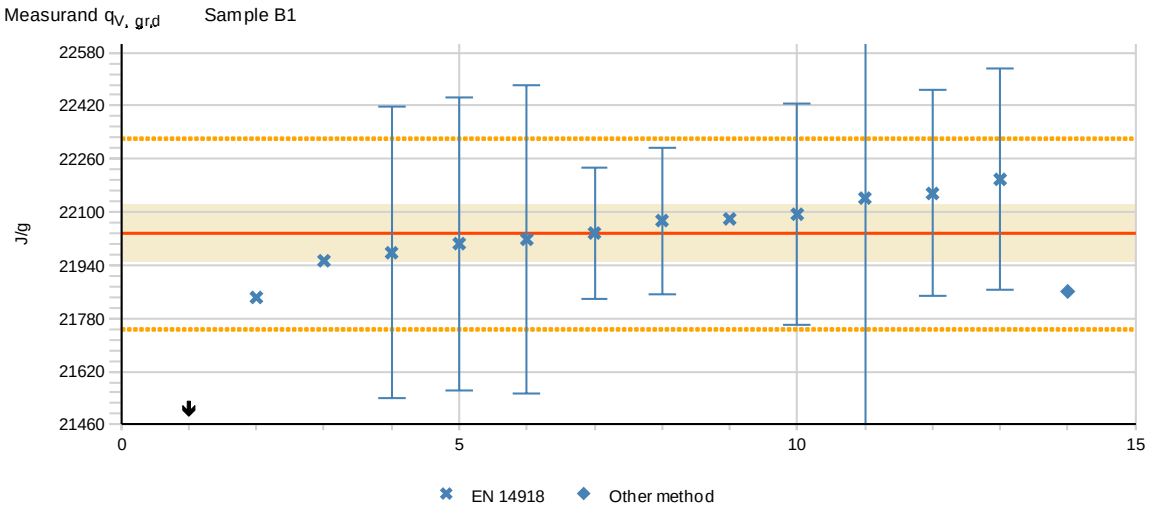

Measurand N_d
Sample B2
w%
0,100
0,075
0,050
0,025
0,000
0
5
EN 15104
EN ISO 16948

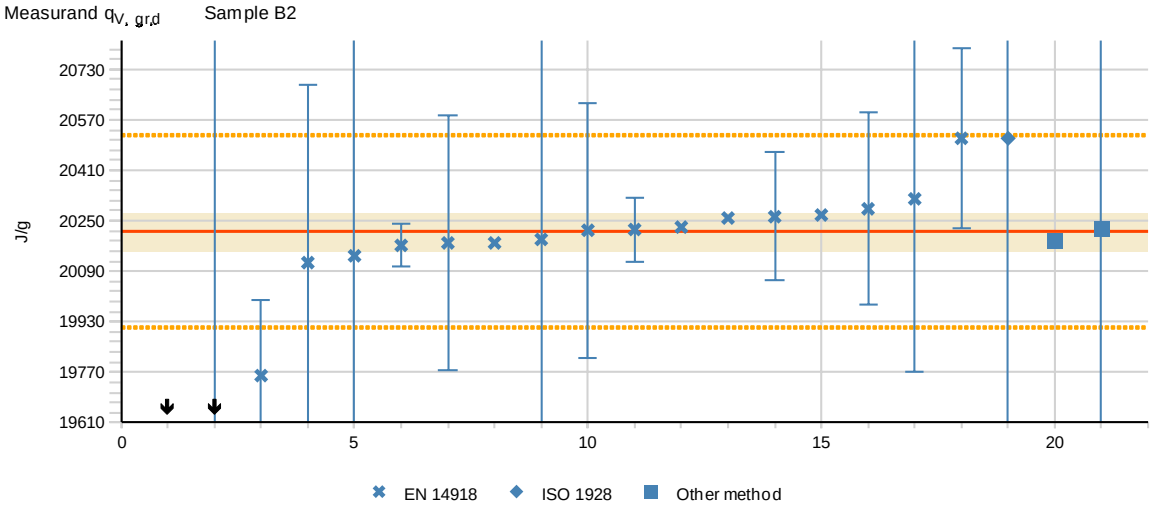

Measurand N_d
Sample K1
w%
2,6
2,5
2,4
2,3
2,2
2,1
2,0
1,9
1,8
0
5
10
EN 15104
ISO 29541
ASTM D 5373

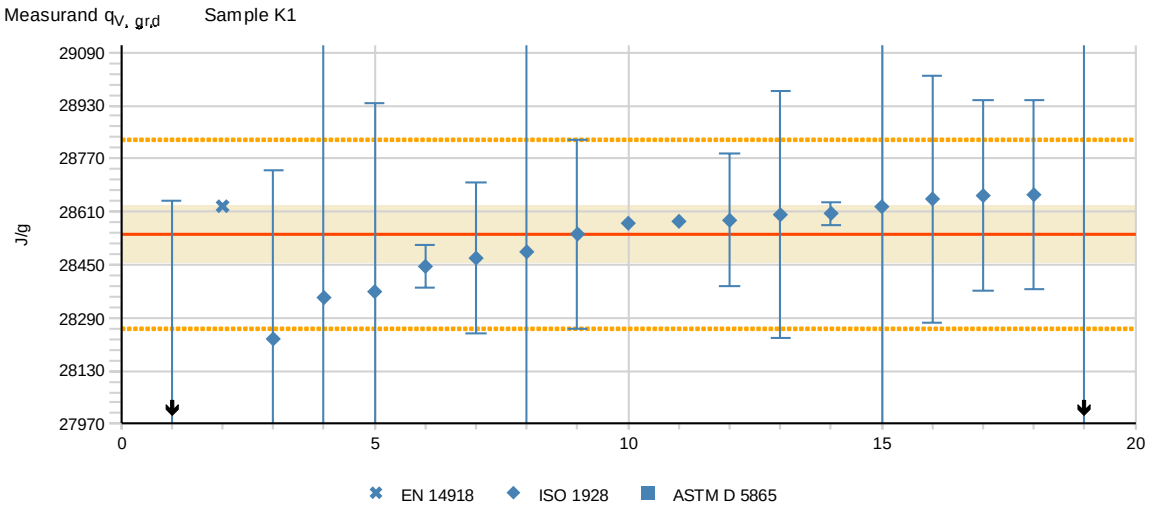

Measurand $q_{p,\ net,d}$
Sample B1
J/g
21340
21180
21020
20860
20700
20540
20380
20220
20060
0
5
10
EN 14918


Measurand $q_{p,\ net,d}$
Sample B2
J/g
19490
19330
19170
19010
18850
18690
18530
18370
18210
0
5
10
15
EN 14918
ISO 1928
Other method

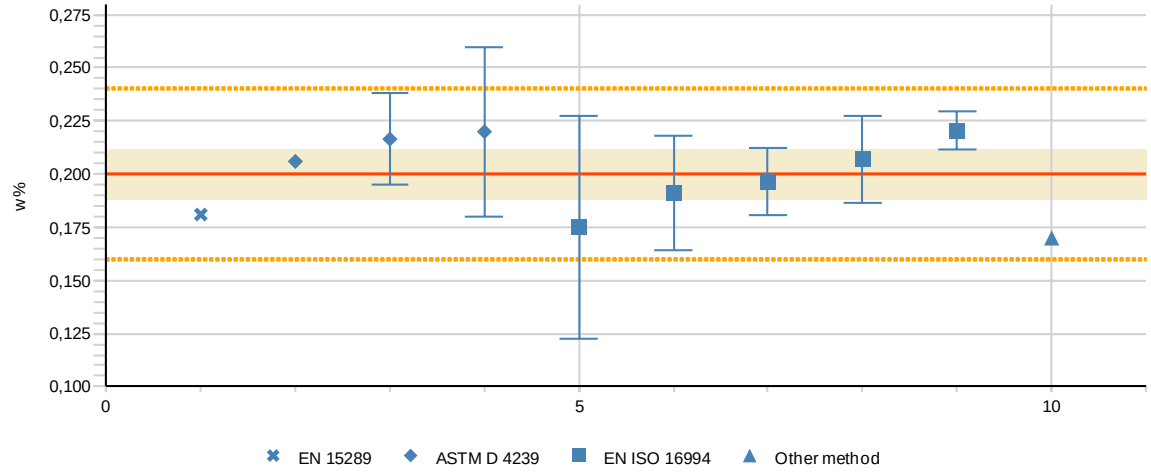

Measurand $q_{p,\ net,d}$
Sample K1
J/g
28130
27970
27810
27650
27490
27330
27170
27010
26850
0
5
10
EN 14918
ISO 1928


Measurand $q_{V,grd}$
Sample B1
J/g
22580
22420
22260
22100
21940
21780
21620
21460
0
5
10
15
EN 14918
Other method

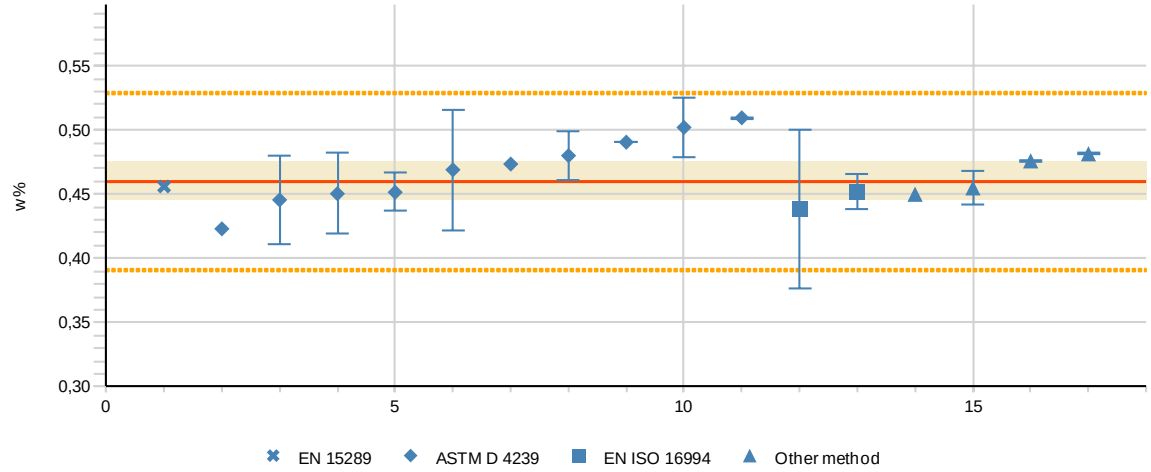

Measurand $q_{V,grd}$
Sample B2
J/g
20730
20570
20410
20250
20090
19930
19770
19610
0
5
10
15
20
EN 14918
ISO 1928
Other method


Measurand $q_{V,grd}$
Sample K1
J/g
29090
28930
28770
28610
28450
28290
28130
27970
0
5
10
15
20
EN 14918
ISO 1928
ASTM D 5865

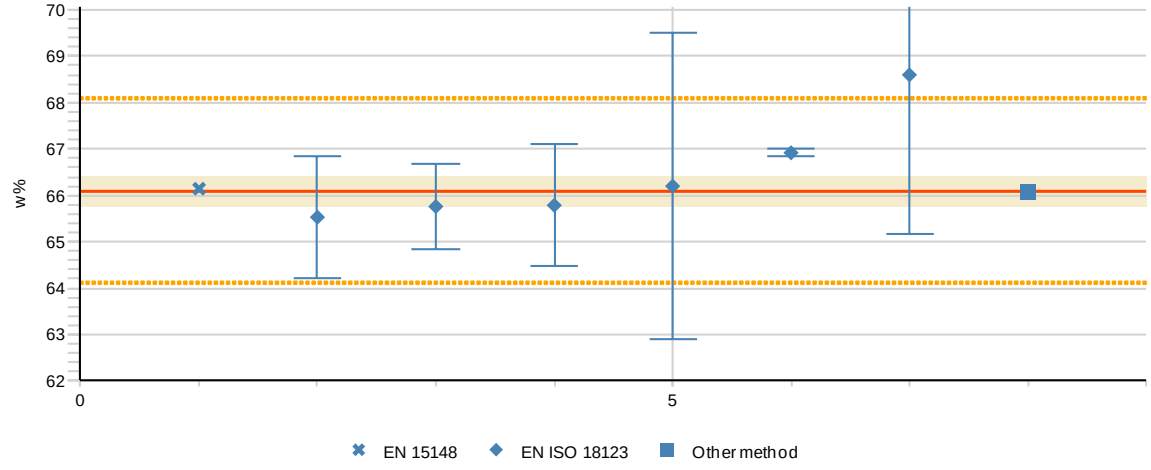
Measurand S_d Sample B1

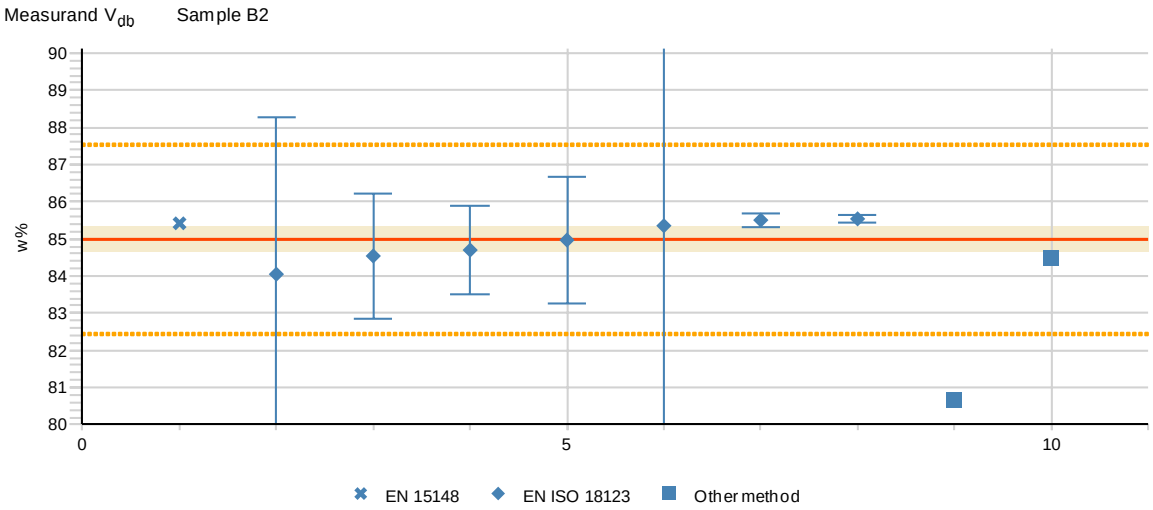


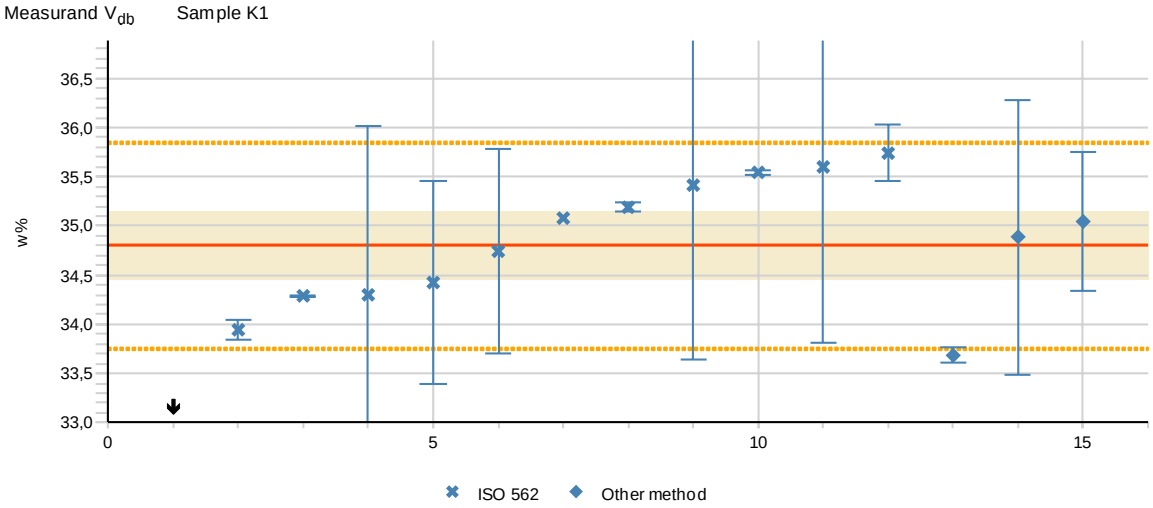
Measurand S_d Sample K1



Measurand V_{db} Sample B1

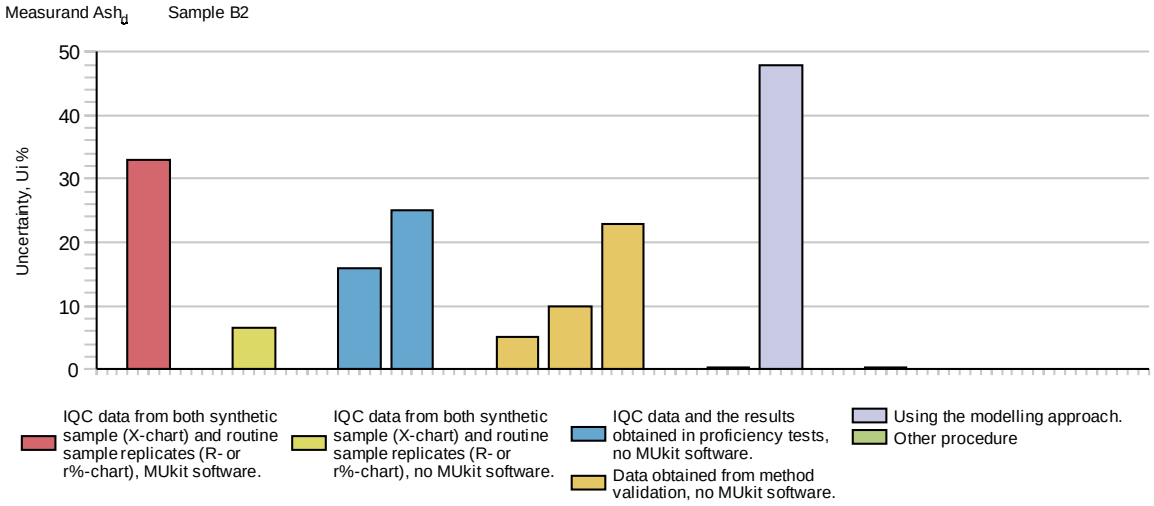


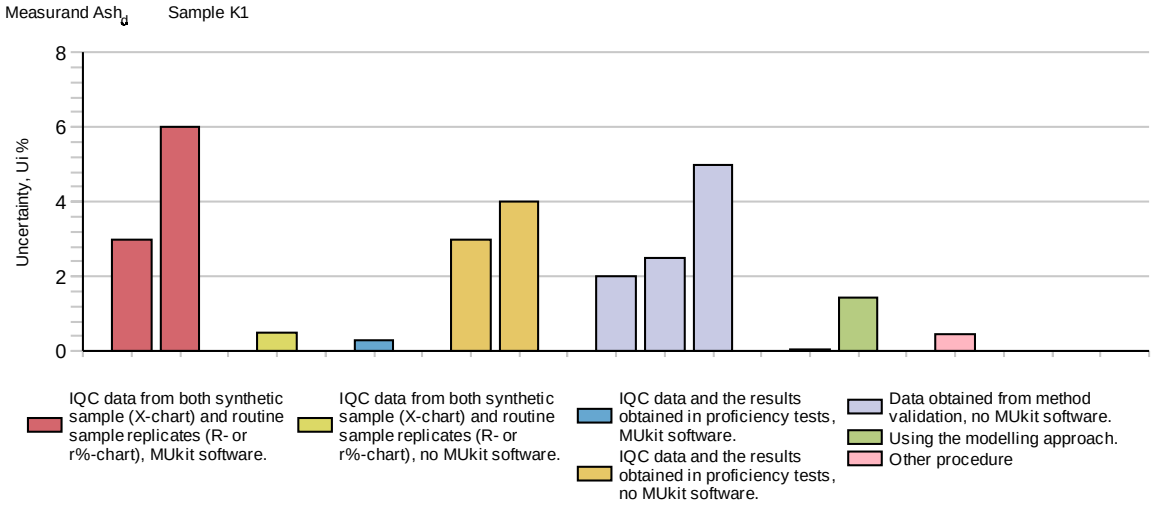

Measurand V_{db}
Sample B2
w%
90
89
88
87
86
85
84
83
82
81
80
0
5
10
EN 15148
EN ISO 18123
Other method

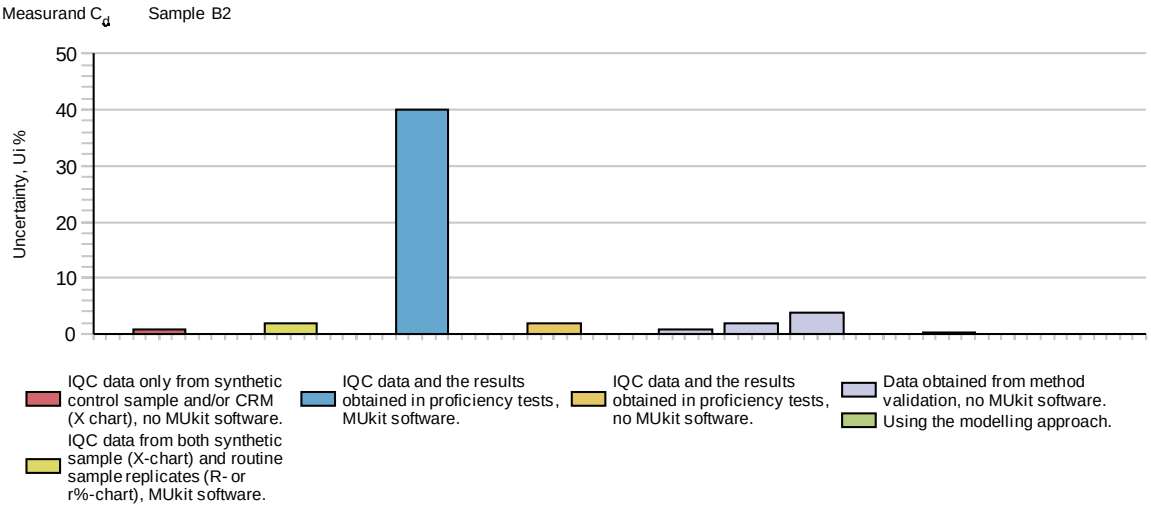

Measurand V_{db}
Sample K1
w%
36,5
36,0
35,5
35,0
34,5
34,0
33,5
33,0
0
5
10
15
ISO 562
Other method

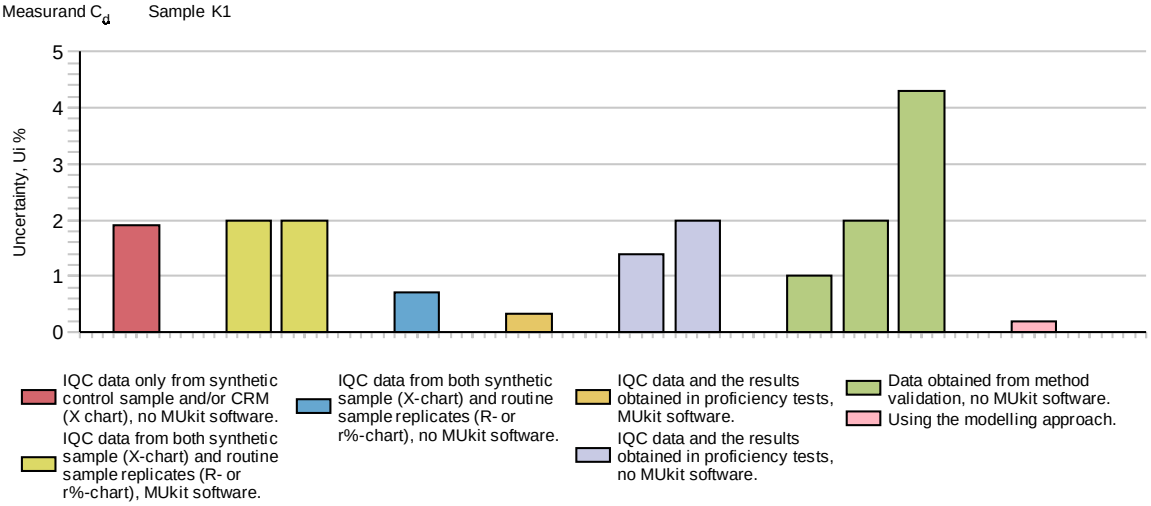
APPENDIX 13: Examples of measurement uncertainties reported by the participants

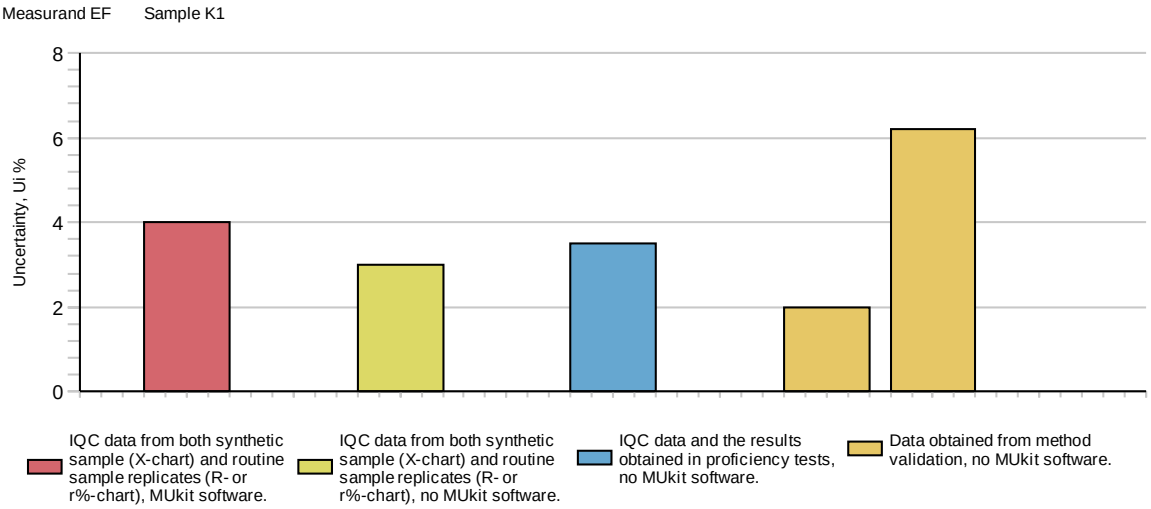
In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level (k=2). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g. between using or not using the MUkit software for uncertainty estimation [29, 30] or using a modelling approach based [31, 32].

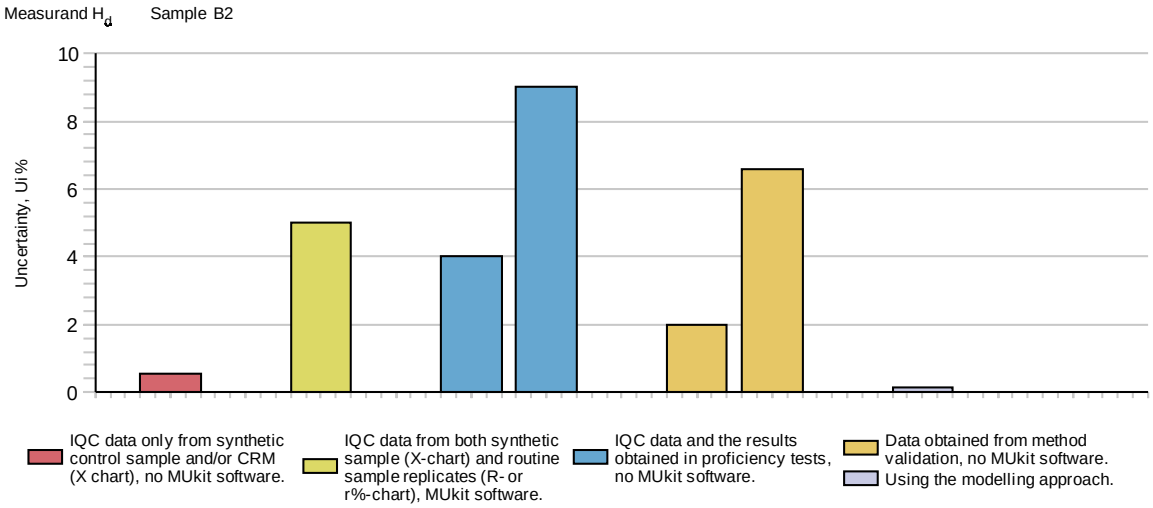


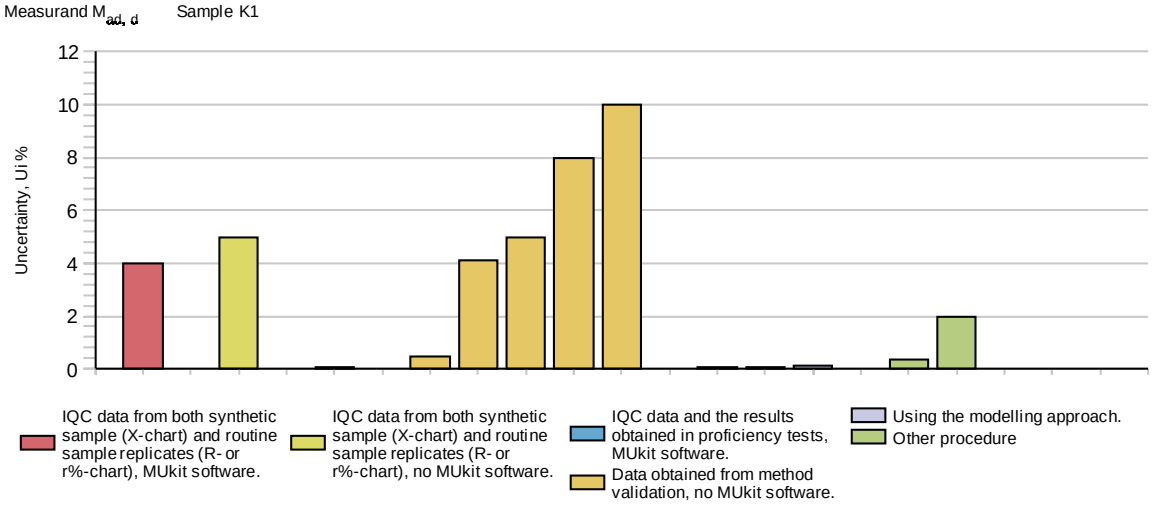


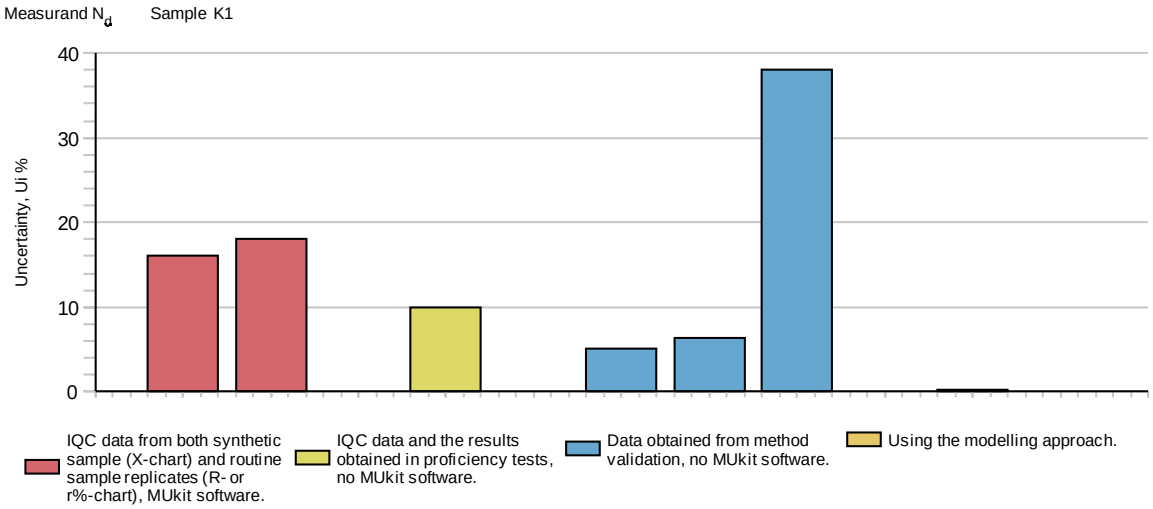

Measurand C_d Sample B2
Uncertainty, Ui %
50
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.

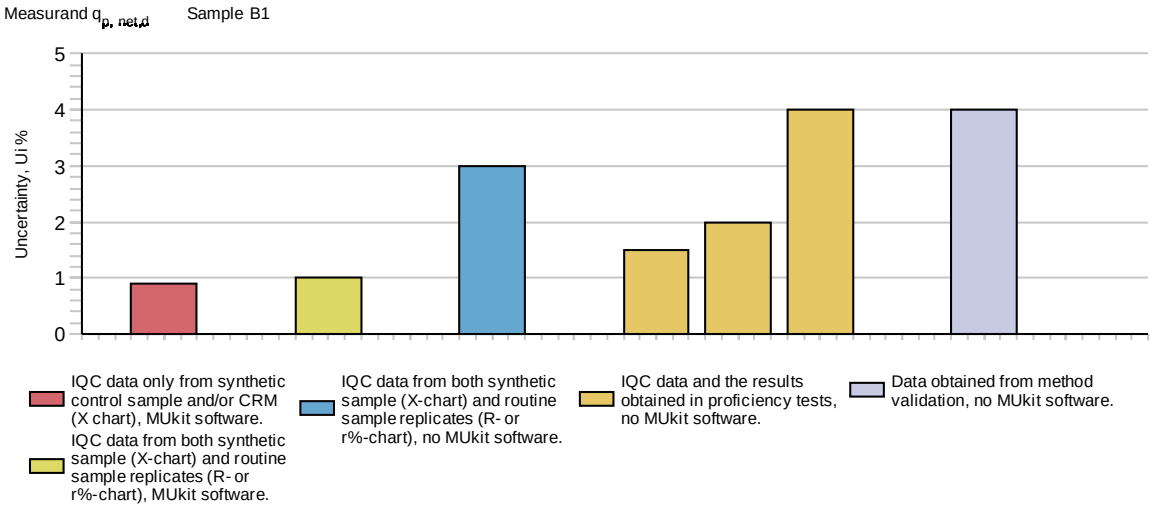

Measurand C_d Sample K1
Uncertainty, Ui %
5
4
3
2
1
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.

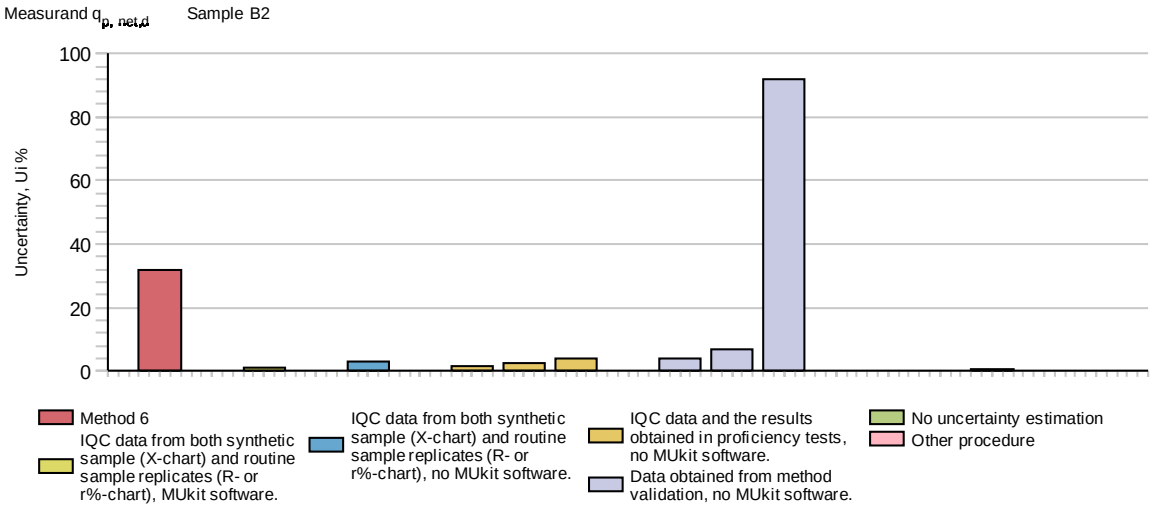

Measurand EF Sample K1
Uncertainty, Ui %
8
6
4
2
0
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.

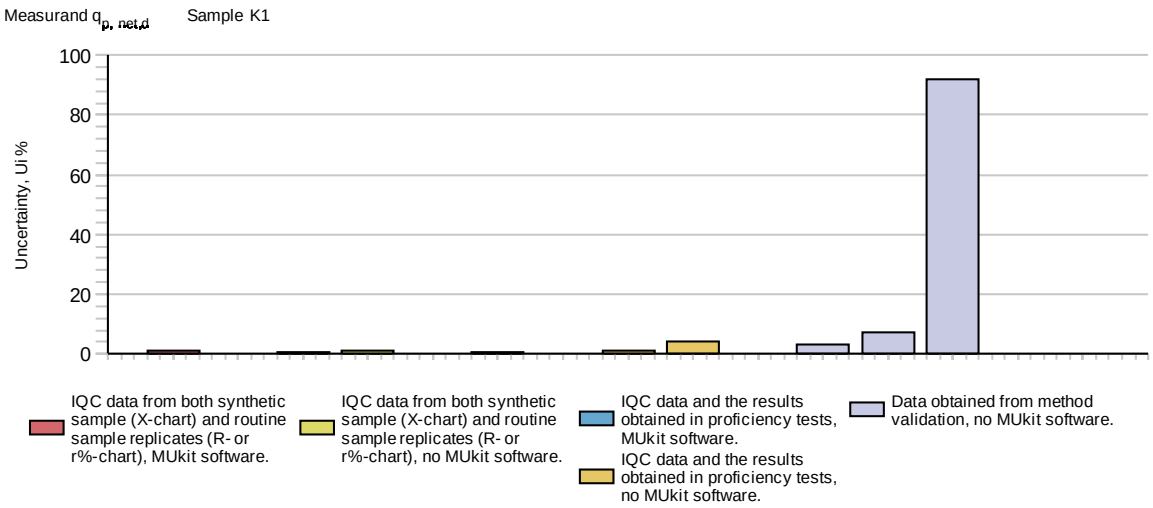

Measurand H_d
Sample B2
Uncertainty, Ui %
0
2
4
6
8
10
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.

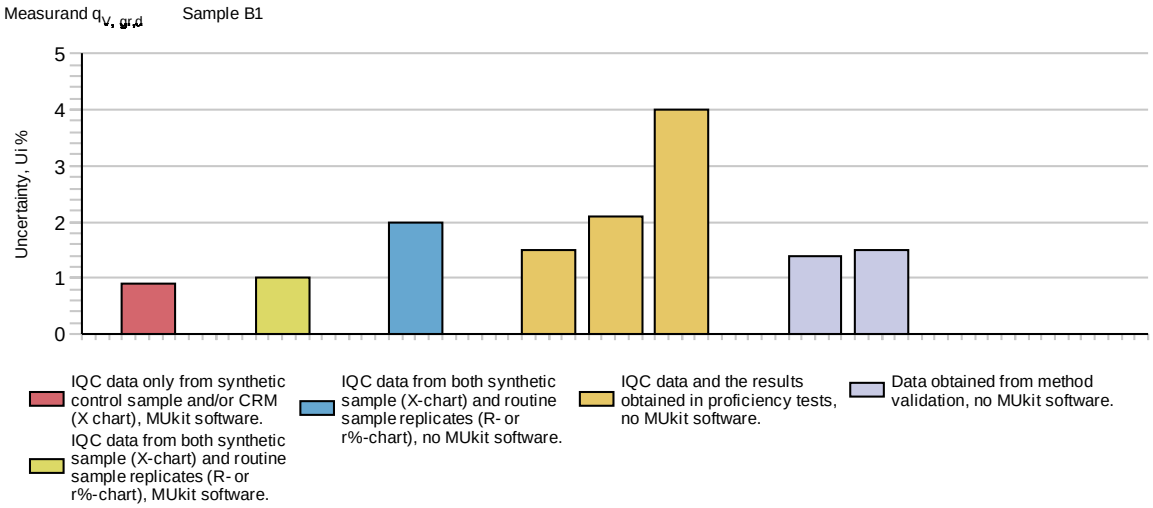

Measurand $M_{ad, d}$
Sample K1
Uncertainty, Ui %
0
2
4
6
8
10
12
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.
Other procedure

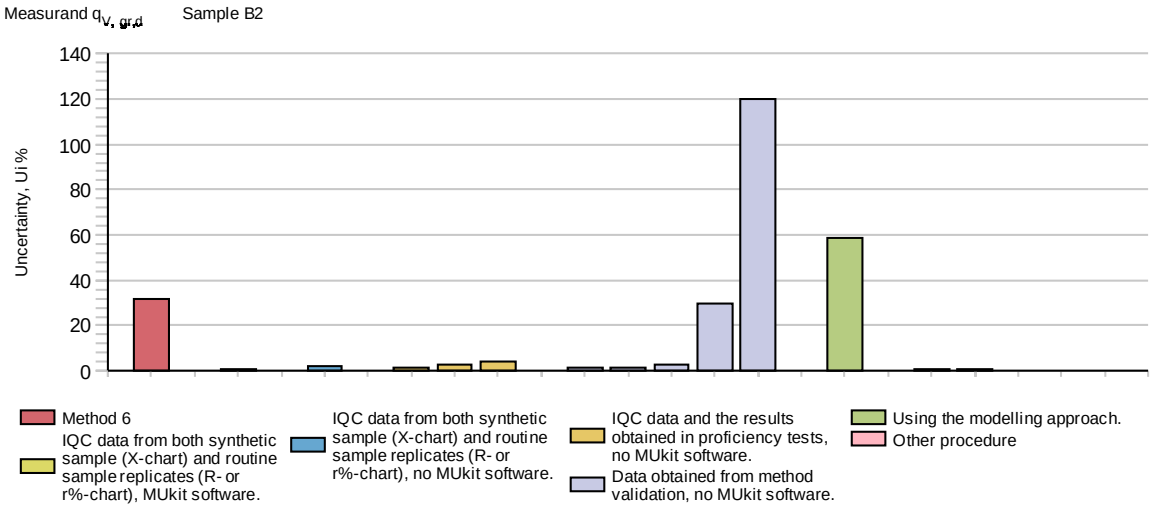

Measurand N_d
Sample K1
Uncertainty, Ui %
0
10
20
30
40
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.

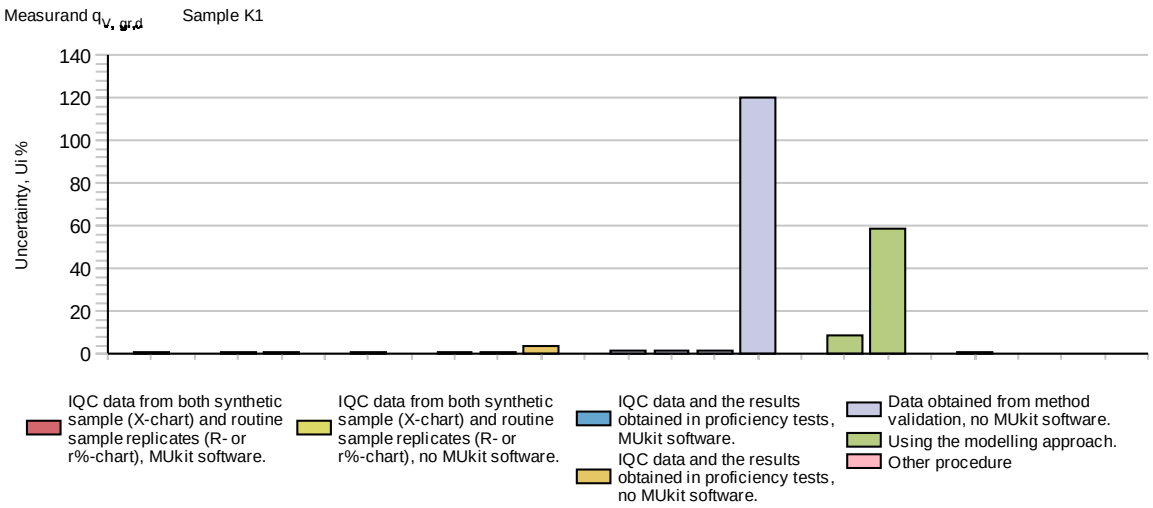

Measurand $q_{p,\ net,d}$
Sample B1
Uncertainty, U i %
0
1
2
3
4
5
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.


Measurand $q_{p,\ net,d}$
Sample B2
Uncertainty, U i %
0
20
40
60
80
100
Method 6
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
No uncertainty estimation
Other procedure


Measurand $q_{p,\ net,d}$
Sample K1
Uncertainty, U i %
0
20
40
60
80
100
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.


Measurand $q_{V,gr,d}$
Sample B1
Uncertainty, U i %
0
1
2
3
4
5
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.


Measurand $q_{V,gr,d}$
Sample B2
Uncertainty, U i %
0
20
40
60
80
100
120
140
Method 6
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.
Other procedure


Measurand $q_{V,gr,d}$
Sample K1
Uncertainty, U i %
0
20
40
60
80
100
120
140
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.
Other procedure

PROFICIENCY TEST SYKE 08/2016

FINNISH ENVIRONMENT INSTITUTE

ISBN 978-952-11-4654-1 (PDF)
ISSN 1796-1726 (online)